

PHOSPHATE UPTAKE BY LATERITIC SOILS

82152

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

VINOD KUMAR MEHTA

to the

DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

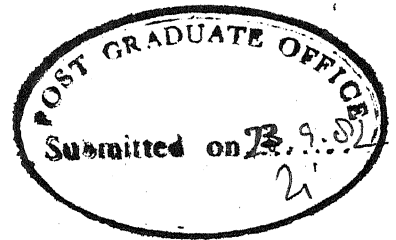
SEPTEMBER, 1982

76 MAY 1984

CENTRAL LIBRARY

Acc. No. **A 82457**

CE-1983-M-MEH-PHO



C E R T I F I C A T E

This is to certify that the present work, entitled
'PHOSPHATE UPTAKE BY LATERITIC SOILS' has been carried out
by Mr. VINOD KUMAR MEHTA under my supervision and the
same has not been submitted elsewhere for a degree.

Raymahashay

BIKASH C. RAYMAHASHAY
Professor
Department of Civil Engineering
Indian Institute of Technology, Kanpur.

A C K N O W L E D G E M E N T S

The author is indebted to his Thesis Supervisor, Dr. B.C. Raymahashay for his valuable guidance and encouragement throughout this work.

The author is grateful to Dr. K.N. Rai of Metallurgical Engineering Department for his permission to work in the Electrochemistry and Corrosion Laboratory.

The help rendered by Dr. K.V.G.K. Gokhale, Dr. D.M. Rao and Dr. Malay Chaudhuri of Civil Engineering Department and Dr. A.K. Biswas of Metallurgical Engineering Department is gratefully acknowledged.

The author is obliged to Mr. P.C. Chaturvedi, Research Scholar at the Geological and Prospecting Institute, Moscow, USSR for supplying the laterite samples from his collection.

Lastly, but not least, the author is thankful to his friends Mr. M. Ramakanth, Mr. Vikas Kaushik and Mr. J. Krishnamurthy for their timely help, and to Mr. N.P. Singh for typing the manuscript.

VINOD KUMAR MEHTA

CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
ABSTRACT	1
CHAPTER I : INTRODUCTION AND OBJECTIVE	3
CHAPTER II : PREVIOUS WORK	
2.1 : LATERITIZATION, LATERITES AND LATERITIC SOILS	6
2.2 : MINERALOGY OF LATERITIC SOILS	7
2.3 : STRUCTURE OF CLAY MINERALS	8
2.4 : THE CLAY COLLOIDS AND CHARGE OVER CLAY PARTICLES	9
2.5 : ANION EXCHANGE CAPACITY OF CLAY MINERALS	11
2.6 : THE IRON HYDROXIDE COLLOIDS	13
2.7 : PHOSPHATE ADSORPTION BY IRON OXIDES	15
2.8 : ADSORPTION OF OTHER ANIONS BY CLAYS, SOILS AND SEDIMENTS	16
2.9 : FERTILIZER RESPONSES ON LATERITIC SOILS	17
CHAPTER III : EXPERIMENTAL PROCEDURES	
3.1 : COLLECTION OF SOIL SAMPLES	21
3.2 : X-RAY ANALYSIS	21
3.3 : REMOVAL OF ORGANIC MATTER FROM SOIL	22
3.4 : DIFFERENTIAL THERMAL ANALYSIS	22
3.5 : ELECTROPHORESIS	22
3.6 : PHOSPHATE ANALYSIS	23

CHAPTER IV	:	RESULTS AND DISCUSSIONS	
4.1	:	GEOLOGY OF LATERITE OCCURRENCES	26
4.1.1	:	DETAILED MINERALOGY OF LATERITIC SOILS	27
4.2	:	PHOSPHATE UPTAKE BY CALICUT LATERITE	30
4.2.1	:	UPTAKE FROM NORMAL PHOSPHATE SOLUTIONS	31
4.2.2	:	UPTAKE FROM ACIDIFIED SOLUTIONS	32
4.2.3	:	MECHANISM OF PHOSPHATE REMOVAL	35
4.3	:	PHOSPHATE UPTAKE BY VARKALA LATERITIC SOIL	39
4.3.1	:	UPTAKE FROM NORMAL SOLUTIONS	39
4.3.2	:	UPTAKE FROM ACIDIFIED SOLUTIONS	40
4.3.3	:	EFFECT OF HIGHER SOIL PROPORTION	41
4.3.4	:	UPTAKE DIFFERENCES OF CALICUT AND VARKALA SOIL	41
4.4	:	ELECTROPHORESIS EXPERIMENT	42
4.5	:	PHOSPHATE UPTAKE BY COMMERCIAL KAOLINITE	43
4.5.1	:	IMPURITIES IN SAMPLE	44
4.5.2	:	UPTAKE FROM NORMAL SOLUTIONS	44
4.5.3	:	UPTAKE FROM ACIDIFIED SOLUTIONS	45
4.5.4	:	LATERITES VERSUS KAOLINITE	46
CHAPTER V	:	CONCLUSION AND FURTHER WORK	
5.1	:	CONCLUSIONS	84
5.2	:	SCOPE FOR FURTHER WORK	85
LIST OF FIGURES			87
LIST OF TABLES			89
REFERENCES			90

ABSTRACT

Laboratory experiments were designed to study phosphate uptake from aqueous solutions by two typical lateritic soils, obtained from Kerala state. The sample from Calicut represents laterites developed over basement rocks. The second from Varkala is from ferruginous soil over younger coastal sedimentary beds.

The efficiency of uptake decreased with an increase in initial phosphate concentration in the range 2 to 50 mg/l PO_4 . However, the Calicut soil showed a relatively high efficiency of 98 to 100 percent compared to 85 percent for Varkala soil. An increase in the efficiency of uptake was observed on acidification of the solution and by increasing soil to solution ratio at 25 to 33°C.

The difference in phosphate uptake by the two lateritic soils was explained by a difference in mineralogy of the two, which in turn was related to difference in their parent rocks. The Calicut soil was found to have a larger proportion of positively charged iron oxides and clay fraction, compared to the Varkala soil. The charge over iron oxide particles was confirmed by a comparative electrophoretic experiment with lateritic soil and commercial kaolinite.

Kinetic interpretations of the removal data showed four stages : (1) Instantaneous removal on surface sites of iron oxides and clay minerals, (2) Saturation of these sites and the first equilibrium stage, (3) gradual removal into the interlamellar sites of halloysite, and (4) saturation with final equilibrium stage.

It is suggested that lateritic soils can be utilized as a barrier against phosphate in waste waters which usually causes eutrophication in reservoirs. At the same time the usually nutrient deficient lateritic soils should be amenable to treatment by phosphate fertilizers.

CHAPTER I. INTRODUCTION AND OBJECTIVE

Phosphate in natural waters as well as in domestic and industrial waste waters has drawn much attention from environmental engineers and geochemists in recent times. This is primarily because this form of elemental P is an important nutrient for plant growth. There are two major aspects of this situation which merit scientific investigations.

On one hand phosphate is ^a 'pollutant' in the ~~sense~~ that its entry into receiving waters causes undesirable algal bloom in a process, called 'Eutrophication' (Fruh, 1967). On the other hand, phosphate-based fertilizers are applied to barren soils in order to make up for their low nutrient level and thereby increase fertility (Robson and Gilkes, 1979).

For pollution control, it is important to maintain the phosphate level below a certain limit so that nutrient supply is less than that required for algal growth. Phosphate removal is a routine process for water treatment and is commonly adopted through chemical and biological means. It has been mentioned that total phosphorus as phosphates should not exceed $50\mu\text{g/l}$ in any stream at the point where it enters any lake or reservoir, or $25\mu\text{g/l}$ within the lake or reserroir. A desired goal for the prevention of plant nuisances in streams or other flowing waters not discharging directly to lakes or impoundments is $100\mu\text{g/l}$ of total P (Train, 1979).

For agricultural practice, using phosphate fertilizers the anion adsorption property of soil minerals is the controlling factor. A negative radical like PO_4^{-3} is 'fixed' on the positive sites on clay and iron oxide colloids. Therefore, soils containing clay minerals and iron oxides e.g. Lateritic soils are expected to be most efficient for phosphate fixation .

Lateritic soil profiles are well known products of chemical weathering in tropical climates. For example, in India, lateritic soils (red soils) occur widely over most of the Penninsular shield, Deccan Traps and many coastal sedimentary rocks.

It should be clear from the above discussions that in such terrains, lateritic soil can serve a dual purpose. It can act as a barrier against disposal of wastes containing dissolved phosphate which are likely to cause eutrophic conditions. At the same time, barren lateritic soils can be reclaimed by application of phosphate fertilizers to meet the demands of agriculture.

The objective of the present work was to investigate the role of the mineral constituents of lateritic soils in the uptake of dissolved phosphate. It was hoped that this information will encourage utilisation of lateritic soils as cheap and easily available material for removal of dissolved phosphate and this will be an improvement over standard

treatment processes like chemical coagulation . At the same time, these data will help understanding of mechanism of phosphate uptake by lateritic soils during the application of phosphate fertilizers.

To achieve these objectives, laboratory experiments were designed to

- (1) Determine the phosphate concentration, remaining in solution after putting a fixed weight of lateritic soil in contact with fixed volumes of standard phosphate solutions, for a desired length of time.
- (2) vary the contact time and thereby to determine the kinetics of phosphate uptake.
- (3) acidify the phosphate solutions in order to create positively charged sites on the soil mineral surfaces for phosphate uptake, and
- (4) compare the uptake capacity of lateritic soil with an iron oxide free material i.e. commercial kaolinite.

CHAPTER II. PREVIOUS WORK

2.1. LATERITIZATION, LATERITES AND LATERITIC SOILS:

The term laterite was first introduced by Buchanan in 1807 to describe red soils of Malabar coast of India which harden on exposure. Today, a weathering process in tropical climates which leads to formation of a surface capping containing an accumulation of sesquioxides (mainly Al_2O_3 and Fe_2O_3) over a variety of rocks is known as 'Lateritization' and the resulting indurated deposit is called as 'laterite'. The soils which are lateritized to varying degrees and contain clay minerals along with sesquioxides are classified as 'lateritic soils'.

Pendelton and Sharasuvana (1946) defined 'lateritic soils' as 'profiles in which there is an immature lateritic horizon from which a true lateritic horizon will develop if appropriate conditions prevail long enough'.

Gidigas (1976) used the term 'lateritic soils' to describe all the reddish residual and non-residual tropically weathered soil, which genetically form a chain of materials ranging from decomposed rock through clay to sesquioxide rich crusts.

2.2. MINERALOGY OF LATERITIC SOILS:

The primary rock and environment, under which the laterite formed are the major controlling factors for the mineralogical composition of laterites. Lateritic soils, however, are by no means limited to particular type of parent material. The following minerals can be present in lateritic soils:

I. Aluminum hydroxides:

- (a) Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, α -alumina trihydrate)
- (b) Bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, β -alumina trihydrate)
- (c) Boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, α -alumina monohydrate)
- (d) Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, β - alumina monohydrate)

Apart from these, noncrystalline hydroxides are also present which do not have definite composition or structure.

II. Iron oxides and hydroxides:

- (a) Hematite, (α - Fe_2O_3)
- (b) Maghemite (γ - Fe_2O_3)
- (c) Goethite (α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)
- Lepidocrocite (γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)
- Ferryhydrite ($(\text{Fe}_5\text{H})_8 \cdot 4\text{H}_2\text{O}$)
- Akaganeite (β - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)

III. Clay Minerals:

- (a) Kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (b) Hydrated Halloysite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
- (c) Meta-halloysite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (d) Montmorillonites or Smeectites, $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$
(Inter layer)
- (e) Illite, $\text{K}_{0-2}\text{Al}_4(\text{Al}_{0-2}\text{Si}_{8-6})\text{O}_{20}(\text{OH})_4$
- (f) Vermiculite, $(\text{OH})_4(\text{Mg}, \text{Ca})_{1-1.4}(\text{Si}_{7-6.6}\text{Al}_{1-1.4})\text{O}_{20} \cdot \text{H}_2\text{O}$
- (g) Chlorites, $(\text{OH})_4(\text{Si}, \text{Al})_8(\text{Mg}, \text{Fe})_6\text{O}_{20} + (\text{Mg}, \text{Al})_6(\text{OH})_{12}$

The above said compositions of kaolinites and halloysites and of montmorillonites are ideal ones with no substitution. However according to the amount of substitution, substituting cation and place of substitution, different members of these families can be recognised.

2.3. STRUCTURE OF CLAY MINERALS:

Kaolinite is a typical two-layer clay containing one gibbsite layer and one hydrated silica layer. A simplified sketch of kaolinite is shown in Fig. 2.1. As indicated, the C-axis spacing in this structure is about 7.2⁰Å. The structural formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Compared to montmorillonite, kaolinite is a non expandable type of clay mineral.

The $4\text{H}_2\text{O}$ form of halloysite, referred as 'hydrated halloysite' has a structure similar to kaolinite, but contains in addition a single molecular sheet of water between the silicate layers (Fig. 2.1). The presence of this water

increases the basal spacing from 7.1Å to 10.0Å. Under electron microscope this species has characteristic tubular shape (Bates et al, 1950). On drying the additional water is readily lost and the structure collapses to 7.1Å. The collapsed form is known as 'metahalloysite'. All intermediate stages between the two limits of hydration exist in nature and they are called as 'Intermediate halloysites'.

Montmorillonite is comprised of a gibbsite layer between two hydrated silica layers, and is designated as a three layer type of clay (Fig.2.1). The minimum C-axis spacing usually amounts to 9.2Å. The C-spacing of montmorillonite, however is quite variable as a result of sorbed water between the layers. (Interlayer or Interlamellar water).

Illite is a three-layer structure being similar to that of muscovite, but is different in that only about 15% of Si is substituted by Al in comparison to about 25% in muscovite. In illite, the charge deficiency due to isomorphous replacement is compensated by K. The C-axis dimension in illite is about 10.1Å (Fig.2.1).

2.4. THE CLAY COLLOIDS AND CHARGE OVER CLAY PARTICLES:

The colloidal solution of clay in water is an example of hydrophobic sols. The particles in clay sols are negatively charged, since they move towards the positive electrode on flow of electric current (Van Olphen, 1963). Like the other sols,

clay sol also does not have a net electric charge, but it is compensated internally by counter ions of opposite sign, thus forming a 'double electric layer'.

The clay particle is an example in which an electric double layer originates from lattice imperfections (Van Olphen, 1963). Grim (1953) suggests that there are three mechanisms believed to be responsible for charge phenomena on clay mineral surfaces. Specifically, these mechanisms are isomorphous replacement, broken bonds and lattice defects.

The creation of negative charge on clay surfaces from isomorphous replacement might occur through substitution of Al for Si in the tetrahedral layer or by Mg for Al in octahedral layer. It is believed that this mechanism is more germane to montmorillonite than to kaolinite with respect to exchange capacity (Grim, 1953; Wayman, 1967).

Many investigators also support the concept that broken bonds along crystalline edges of clay platelets are also an important mechanism (Marshall, 1949; Grim, 1953). Bonds may be broken in either the tetrahedral or octahedral layer. In the octahedral layer the situation would involve:



If the severance is between Al and O, then a site is created with a positive charge. If between O and Al, then the site becomes negative as a result of the exposed ion. (generally of an OH ion). The same type of reasoning can be applied to the tetrahedral layer where in the bonding is



In all probability it is not unreasonable to predict that both positive and negative sites should occur along the edge.

Van Olphen (1963) proposed a dual charge in terms of electric double layer theory. It is suggested that a negative double layer exists along the faces and that a positive double layer occurs on the particle edge, notwithstanding the overall effect of net negative charge (Fig.2.2). If this evidence is correct, the overall net negative charge readily explains the higher cationic exchange capacity on faces in comparison to the observed low values of anionic exchange occurring most likely at the edges.

2.5. ANION EXCHANGE CAPACITY (AEC) OF CLAY MINERALS:

The investigations of anion exchange in clay materials have been to a considerable extent associated with studies of the adsorption of phosphate by soils. There seem to be two, and possibly three types of anion exchange in the clay minerals, (Grim, 1953).

1. Replacement of OH ions, as has been suggested by many authors for the phosphate adsorption by kaolinite. It has been shown that the liberation of hydroxyls caused a well marked increase in the alkalinity of the suspensions. In the case of exchange due to replacement of OH ions, the extent of the reaction depends on the accessibility of the OH ions, and in general the only factor preventing complete substitution is the fact that many OH ions are within the lattice and, therefore, not accessible.

2. Anions such as phosphate, arsenate, borate, etc. which have about the same size and geometry as the silica tetrahedron may be adsorbed by fitting on to the edges of the silica tetrahedral sheets and growing as extensions on these sheets. Other anions such as sulphate, chloride, nitrate etc., because their geometry does not fit that of the silica tetrahedral sheets, can not be so adsorbed.

3. A third manner of anion exchange has been suggested that the clay minerals may have anion-exchange spots as well as cation-exchange spots on basal plane surfaces. Such active anion-exchange positions would be due to unbalanced charges within the lattice i.e. an excess of aluminum in the octahedral positions. Table 1 gives the anion-exchange capacity for some of the clay minerals.

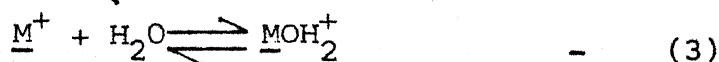
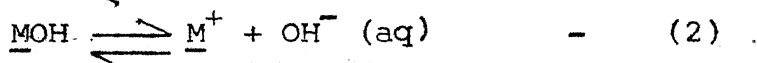
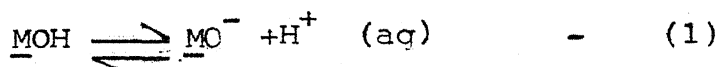
Table-1 Anion exchange capacities (in me/100g) of clay minerals (Grim, 1953)

Montmorillonite	23 - 31
Beidellite	21
Nontronite	12 - 20
Saponite	21
Vermiculite	4
Kaolinite	6.6 - 20.2

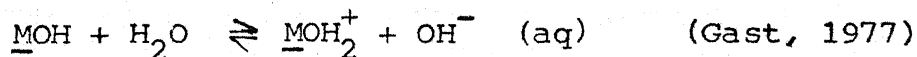
2.6. THE IRON HYDROXIDE COLLOIDS:

In nature ferric hydroxide most commonly forms in a faintly acid environment, and so has a positive charge. But the charge can be negative, if solution is alkaline (Krauskopf, 1967).

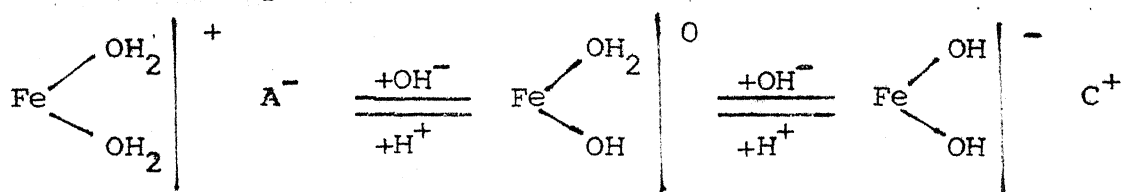
Exposure of oxide or hydroxide particles to water generally results in physical and chemical adsorption of water on the surfaces. Chemical adsorption differs from physical adsorption in that H_2O is split into H^+ and OH^- during adsorption to form an hydroxylated surface. (Schwertmann and Taylor, 1977). Charge can develop over these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- ions. These reactions can be written as follows, where under-scored symbols refer to the species following part of the surface:



Since the probability of bare M^+ existing at the surface is small, the basic dissociation or formation of a positively charged site probably occurs through a combination of reactions (2) and (3) i.e.



In both the above mechanisms, the H^+ and OH^- ions establish the surface charge and thus charge is pH dependent. The surface charge is created by an adsorption or desorption of H^+ (or a desorption or adsorption of OH^- , respectively) in the potential determining layer consisting of surface O, OH and OH_2 groups. H^+ and OH^- are therefore called 'potential determining ions'. The following model has been proposed (Schwertmann and Taylor, 1977).



Thus an excess of surface charge of the potential determining layer is balanced by an equivalent amount of anions (A^-) or cation (C^+), located in the outer part of an electric double layer.

Summer (1962) reported that removal of iron oxides from red soils resulted in a decrease in positive charge particularly at low pH. This supports the view that iron oxides coating clay surfaces carry a positive charge.

The pH at which equal amounts of H^+ and OH^- ions are adsorbed is called the zero point of charge (ZPC). Values recently reported for the ZPC of synthetic hematite and goethite lie in the range of pH 7.5 - 9.3 (Schwertmann and Taylor, 1977). The ZPC values are generally lower for natural samples than those found for the synthetic ones.

2.7. PHOSPHATE ADSORPTION BY IRON OXIDE:

Specific adsorption of phosphate by iron oxides is most widely accepted and is an important concept in soil and environmental studies. The amount of a particular ion adsorbed depends mainly on its concentration in, and the pH of, the equilibrium solution. At a given pH, adsorption increases with increasing concentration.

Bowden et al (1974) have shown an increase in phosphate adsorption with decreasing pH. To them, this is due to an increasing ratio of $\text{OH}_2^+/\text{OH}^-$ surface groups.

In contrast to adsorption mechanism, Kittrick and Jackson (1956) suggest that chemical precipitation is the principal mechanism in phosphate fixation by iron oxides and clays. The colloidal iron oxide particles and thin Al hydroxide films react with phosphate at room temperature to form PO_4 precipitates, which are readily observable under the electron microscope a few minutes after treatment.

According to some authors (reviewed by Wild, 1950), retention of phosphate by iron oxides follows the Freundlich adsorption isotherm. Others, however, contend that compliance with Freundlich equation is not restricted to adsorption and does not rule out precipitation.

McLaughlin et al (1981) concluded from their studies that the amounts of inorganic P sorbed by a range of Fe- and Al- containing components varied appreciably and decreased from gels to crystalline substances.

sree Ramalu et al (1976) as well as Kuo and Mikkelsen (1979) reported that phosphate fixation is controlled by pH and the proportion of crystalline versus amorphous iron oxides.

2.8. ADSORPTION OF OTHER ANIONS BY CLAYS, SOILS & SEDIMENTS:

With increasing use of anionic detergents, the anion exchange capacity of clays has been used to remove surfactants like ABS (Alkyl Benzene Sulphonate). Wayman (1967) showed that common clay minerals like kaolinite, illite and montmorillonite have similar ABS uptake. Fink et al (1972) found that soils high in free iron oxide are best suited for ABS removal.

Behaviour of anionic dyes is similar to detergents. Kinetic studies by Sethuraman and Raymahashay (1975) showed that kaolinite and montmorillonite have similar rates of sulphur blue adsorption. This was explained by the fact that the adsorption sites are confined to particle edges for both minerals. Sethuraman and Raymahashay (1980) also reported that in contrast to cationic dyes, adsorption of anionic dyes was entirely irreversible and there was no effect of solution pH.

Significant results have also been obtained in virus-clay systems. In the pH range of normal waters, viruses are negatively charged (Drewry and Eliassen, 1968). Under normal circumstances, therefore, negative clay surfaces are

ineffective for virus removal. On the other hand, presence of positively charged iron oxide colloids apparently changes the situation. For example, Koya and Chaudhuri (1976) found that the bacterial virus MS2 phage was removed to a much greater extent by Kerala laterite compared to Kanpur silt.

Some data are also available on the fate of pesticides in soil zones. Huang and Liao (1970) conducted a series of experiments on the adsorption of DDT, Dieldrin and Heptachlor on clay minerals. The Kinetic data were interpreted by a model of interlayer diffusion in montmorillonite. This behaviour was not observed for kaolinite and illite.

2.9. FERTILIZER RESPONSE ON LATERITIC SOILS:

In many parts of the world, lateritic soils have not been developed for agriculture.

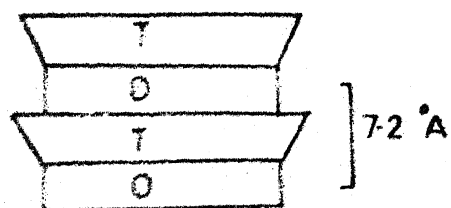
Robson and Gilkes (1979) point out that low level of nutrient elements in the primary granite combined with prolonged deep-weathering and crystallisation of Kaolinite and sesquioxides have resulted in a generally poor nutrient status of the lateritic soils of Australia.

The major features which affect initial fertilizer applications are:

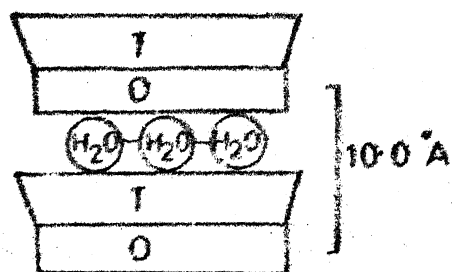
- (1) low nutrient level in virgin soil ($P\% = 0.01$)
- (2) High Fe, Al oxides and hydroxides in soils which adsorb added anions.
- (3) Heavy rain, which leaches soluble minerals

- (4) Low organic matter content which results in low Nitrozen supply.
- (5) High Quartz, Kaolinite and sesquioxides along with low organic matter result in low CEC (10 meq/100 g)

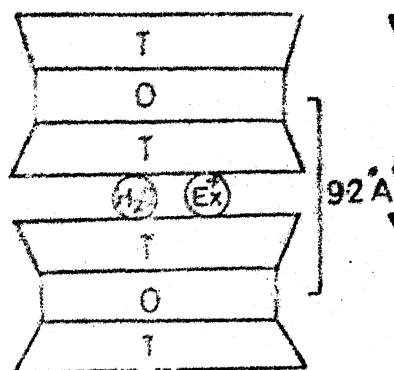
In a glass house trial experiment, it was also observed that sandy kaolinite rich soil has lower P adsorption capacity compared to laterite.



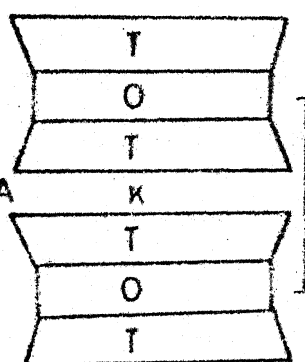
(a) KAOLINITE



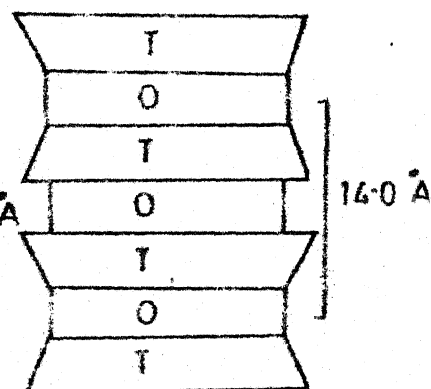
(b) HYDRATED HALLOYSITE



(c) MONTMORILLONITE



(d) ILLITE



(e) CHLORITE

T Si-O TETRAHEDRAL LAYER

O Al, Mg-O, OH OCTAHEDRAL LAYER

(Ex⁺) EXCHANGEABLE CATIONS

Fig. 2.1 - Structure of Clay Minerals

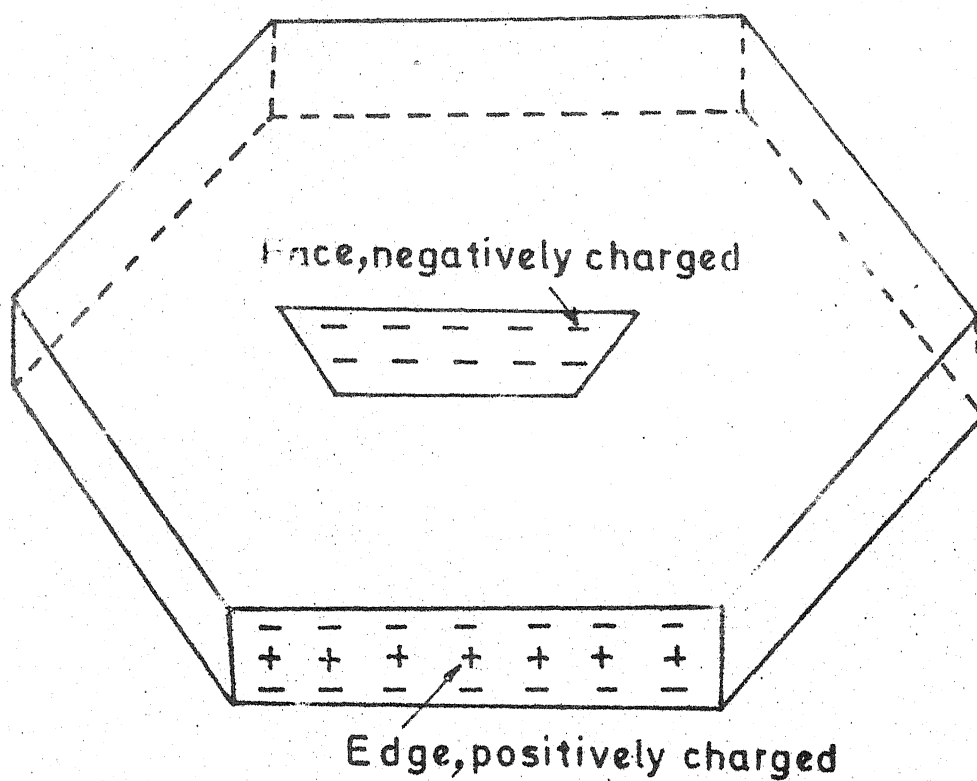


Fig. 2.2 - Schematic Diagram of Dual Charge on a Kaolinite Particle.

(Wayman, 1967)

CHAPTER III. EXPERIMENTAL PROCEDURES

3.1: COLLECTION OF SOIL SAMPLES:

The lateritic soil samples were obtained from two typical profiles in Kerala -

- (a) Laterites capping Precambrian Charnockites and biotite-gniesses in the midland region near Calicut, and
- (b) Laterites, covering Tertiary sandstones near Varkala, a coastal town.

The kaolinite sample was obtained from the collection of the Engineering Geology laboratory, I.I.T., Kanpur.

3.2: X-RAY ANALYSIS:

To determine the mineralogy of clay fraction and for identification of Fe- and Al- minerals, oriented slides of lateritic soils were prepared. For this, some amount of the soils was mixed with distilled water in a cylinder and heavier fraction (Quartz etc.) was allowed to settle for about half an hour. Middle fraction of the clay suspension was taken out by a pipette and spread over a glass slide. The slide was allowed to dry at room temperature. This technique lets the flaky particles to orient themselves parallel to their basal planes, and x-ray identification of the basal peak is easier.

A slide of Varkala soil was exposed to glycol vapour overnight in a dessicator for investigations of swelling-clay minerals.

Kaolinite was examined in powder form in a sample holder.

All the samples were investigated by x-ray diffraction with GEC XRD-5, 30KV X-Ray diffractometer using $\text{CuK}\alpha$ radiations.

3.3: REMOVAL OF ORGANIC MATTER FROM SOIL:

For removal of organic matter, soil suspension was prepared by mixing some amount of soil with water in a beaker. The suspension was heated at about 80°C and small amounts of 30% Hydrogen peroxide (H_2O_2) were added. Alcohol was added from time to time to control frothing.

3.4: DIFFERENTIAL THERMAL ANALYSIS:

Differential Thermal Analysis (DTA) of Varkala soil; the natural as well as that free from organic matter was carried out. Derivatograph - MOM, thermal analyser was used with a heating rate of $10^\circ\text{C}/\text{min}$. through a range from room temperature to 1000°C .

3.5: ELECTROPHORESIS

Beltronix D.C. Power Supplier equipped with essential accessories was used at a potential difference of 135 volts and

lateritic soils and kaolinite were subjected to electrophoresis. Current was flown for a duration of 3 minutes. Particle size of the soil samples and Kaolinite was less than .044 mm.

3.6: PHOSPHATE ANALYSIS:

Pure orthophosphate solutions of known concentrations were prepared by dissolving appropriate amounts of Potassium di-hydrogen ^{Phosphate} (KH_2PO_4) in distilled water. Whenever needed, solutions were acidified with 1 : 1 HCl acid to bring down pH of the solutions to the desired value. Phillips PR9405M precision pH meter was used for pH measurements.

0.5 g of oven-dried soil, particle size varying from 0.18 to 0.25 mm, was mixed each time in 50 c.c. of phosphate solution of known concentration and initial pH. Suspension was stirred for 5 minutes by magnetic stirrer and allowed to settle for 10 minutes. pH was measured.

After the desired contact time, suspension was stirred and allowed to settle for the same duration as earlier and final pH reading was taken. This suspension was filtered, using whatman 42 filter paper and centrifuged by 'SERVALL' small angle centrifuge, type XL, at a speed of 3000 RPM. Decanted solution was stored for determination of final phosphate concentration, after pH measurement.

Final phosphate concentrations were determined by colorimetric stannous chloride method using an acid ammonium molybdate reagent. Colours were read in a SYSTRONICS 103 spectro colorimeter at a wavelength of 690 nm. Calibration curves were prepared for each run using appropriate phosphate standards. (Fig.3.1)

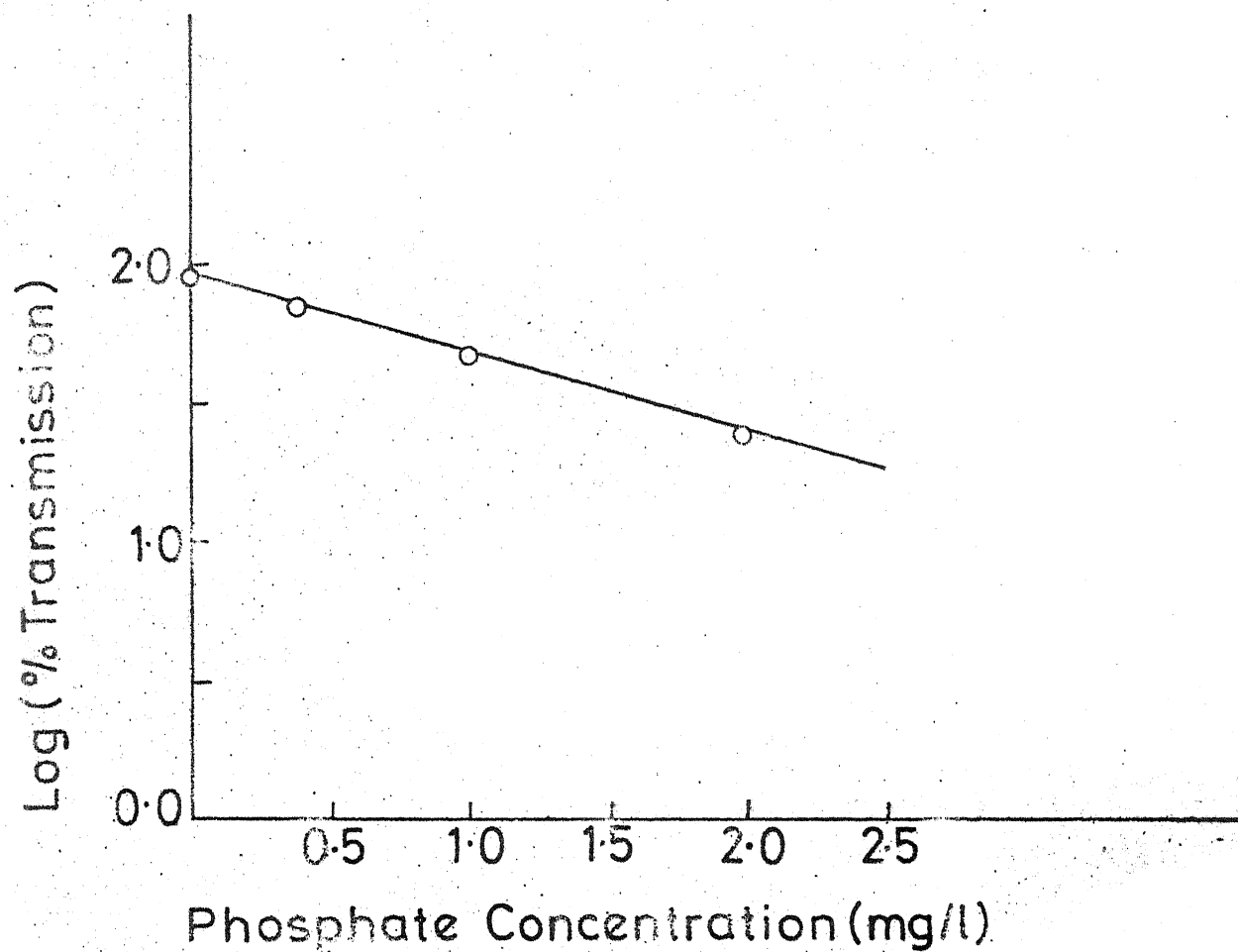


Fig. 3.1 - Typical Standard Curve for Phosphate Determination.

CHAPTER IV. RESULTS AND DISCUSSIONS

4.1. GEOLOGY OF LATERITE OCCURRENCES:

Three stratigraphic horizons of laterite have been recognised in Kerala. These are (1) Laterite over Precambrian basement, (2) Laterite over Tertiary (Miocene - Pliocene) sedimentary rocks, and (3) Laterite over unconsolidated recent (Quaternary) coastal sands and alluvium. (Mallikarjuna et al., 1979). The first horizon is the thickest with depth varying from 1 to 10 m. These profiles occur extensively in the Midland region at the foot hills of Western Ghats. The second and third types occur in the coastal plain. The outcrops are local and variable in thickness.

The Calicut sample represents Laterite over basement. It was obtained from the campus of the Centre for Water Resources Development and Management. The bed rock is composed of high grade metamorphic rocks like charnockites and biotite-gneiss. The soil is deep red in colour.

The Varkala sample comes from ferruginous soil profiles near the town. It represents laterite over Tertiary Warkalli beds consisting of sandstones, clay and carbonaceous shale. The colour is pale brown indicating lesser iron content than the Calicut sample. The grain size is coarse.

Fig.4.1 is the geologic map of Kerala state, which shows geological formations around the localities from where samples were collected.

4.1.1. DETAILED MINERALOGY OF LATERITIC SOILS

Each of the two lateritic soil samples was subjected to detailed mineralogical investigations. Microscopic studies were aimed to investigate mineralogy of coarser fraction of the two soils, whereas techniques like x-ray Diffraction Analysis, and Differential Thermal Analysis helped in easier recognition of different clay minerals and their relative abundance in the soils.

(a) CALICUT SOIL:

A sketch of microscopic view of coarser fraction of the calicut soil, as it appears under a binocular microscope is shown in fig.4.2. Broken crystals of quartz, occasionally of feldspar and dark minerals were recognized. Presence of feldspar was interpreted from its transparency and flawless cleavage. Relative abundance of feldspar was much less in comparison to quartz, present in maximum amount. In abundance, quartz was followed by different iron oxides which appeared with reddish-brown colour and earthy lusture. Maghemite, an iron oxide was recognised from its jet-black colour and crystal shape. Later on, Maghemite was confirmed by virtue of its magnetic property.

X-ray analysis revealed the presence of kaolinite, intermediate halloysite, chlorite, gibbsite, goethite, maghemite and feldspar. A sketch of X-ray diffraction pattern of Calicut soil, after quartz removal is shown in fig.4.3. Diffraction peaks at spacings ranging from 8.11 Å to 11.32 Å were interpreted to be due to halloysite of intermediate hydration between metahalloysite and hydrated halloysite. Its composition can be represented by $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (2+X)\text{H}_2\text{O}$ where $0 < X < 2$. Presence of halloysite in Calicut soil has also been confirmed by Rao and Raymahashay (1981) from characteristic tube shaped crystals in electron micrographs. They also reported kaolinite, goethite and gibbsite from the soil. A comparative look of relative heights of X-ray peaks leads to the conclusion that kaolinite and Chlorite are in maximum abundance, followed by gibbsite, which in turn is followed by maghemite and goethite. Intermediate halloysites are still lesser, whereas feldspar is present in least amount, as indicated by only one peak of it with very low intensity.

(b) VARKALA SOIL:

Presence of abundant quartz, along with feldspar and much less amount of iron oxides was revealed on bringing the coarser fraction of Varkala soil under binocular microscope (Fig.4.4). Methods of interpretation were same, as used for the calicut soil. Pale brown colour of this soil can be attributed to the relatively much lesser abundance of iron oxides.

A sketch of X-ray diffraction pattern of this soil is shown in fig.4.5. From the interplaner spacing (d) values, presence of kaolinite, chlorite, Intermediate halloysites, quartz, feldspar and goethite was confirmed.

Relative intensities of different peaks led to the conclusion that kaolinite was in maximum abundance, along with chlorite, and followed by intermediate halloysites, feldspar and quartz.

To confirm the nature of clay mineral, due to which the 14.4 Å peak appeared, glycolated sample was also subjected to X-ray analysis. No shift of this peak confirmed absence of montmorillonite, or in other words, presence of chlorite.

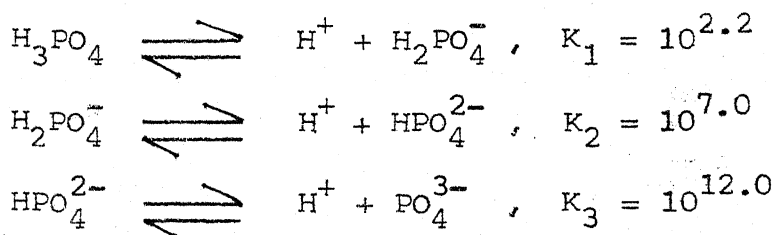
Appearance of endothermic peak at 630°C during Differential thermal analysis further confirmed presence of Kaolinite (Fig.4.6). A loss in weight at this temperature, shown by thermogravimetry curve, is due to dehydroxylation of Kaolinite and hydrated iron oxides.

Comparison of the calicut soil with the Varkala soil revealed mineralogical differences of their parent rocks. Calicut soil is much richer in sesquioxide content than Varkala soil, whereas, on the other hand, the latter contains feldspar in greater abundance. This is most obvious, since Varkala soil is product of sandstones and Calicut soil has resulted from charnockites and biotite-gneisses, which by themselves are rich in iron content.

4.2. PHOSPHATE UPTAKE BY CALICUT LATERITIC SOIL:

To go in depth of mechanism and capacity of phosphate uptake, fixed weights of Calicut lateritic soil were kept in contact with phosphate solutions of different initial concentrations for different contact times. Thus, Batch Experiment method was adopted in the present work.

'Normal phosphate solutions' as well as 'Acidified phosphate solutions' were kept in contact with the soil. These terms have been explained in the next sections. At the present moment it is also worth mentioning that acidification of the solutions not only causes a fall in their pH, but also changes orthophosphate species, although as a whole amount of total phosphates does not change. Following are the reactions with their dissociation constants which determine the pH range, in which a particular phosphate species exists.



In the pH range of the present experiments (3.5 to 7.8) the predominant orthophosphate species will be H_2PO_4^- at low pH and HPO_4^{2-} at higher pH values. It is also obvious that the mechanism and efficiency of phosphate removal will depend on the type of phosphate species in the solution.

However, for analytical purposes the phosphate concentrations are expressed in terms of total orthophosphate as mg/l PO_4 .

4.2.1. UPTAKE FROM NORMAL PHOSPHATE SOLUTIONS:

In the present context, the term 'Normal phosphate solution' refers to a solution prepared by dissolving a known weight of KH_2PO_4 in distilled water. The pH depends on the strength of the solution and no attempt was made to change its natural pH value.

Table 2 to 6 show variations in the pH of normal phosphate solutions after different contact times, apart from final phosphate concentrations and amount of phosphate removed. A decrease in the final phosphate concentration is accompanied by a rise in the final pH of the solution, indicating a continuous increase in the hydroxyl ions concentration. From the data of above mentioned table, figures 4.7 and 4.8 have been drawn.

The efficiency of phosphate removal (e) can be defined as

$$e = \frac{P_i - P_F}{P_i} \times 100 \quad (1)$$

where P_i = initial phosphate concentration,

and P_F = final phosphate concentration

The phosphate uptake capacity which is an apparent 'Anion Exchange Capacity' (AEC) of a material can be defined as 'amount of anions expressed as milliequivalents, exchanged by 100 grams of that material'. In the present work, taking into consideration volume of solution (50 ml) and weight of soil (0.5 g) following relationship can directly give AEC in me/100 gms.

$$\text{AEC (in me/100 g of soil)} = \frac{\text{Amount of phosphate removal (mg/l)} \times 10}{32} \quad (2)$$

From the above two relationships; (1) and (2), efficiency of removal for different initial phosphate concentrations, and AEC for 50 mg/l normal phosphate solution have been calculated (Table 7). This table clearly shows dependence of efficiency on initial phosphate concentration. An increase in initial concentration reduces the efficiency of removal. The maximum phosphate uptake capacity is in the range reported for AEC of Kaolinite type clay minerals (Carroll, 1959).

4.2.2. UPTAKE FROM ACIDIFIED SOLUTIONS:

Term 'Acidified phosphate solution' in the present work has been used for the solution of which pH value was brought down by dropwise addition of hydrochloric acid. The pH value of solution was brought down to 3.5 in every case.

Tables 2 to 6, show variations in the pH of acidified solutions, as well as final phosphate concentrations and amounts of phosphate removal in different contact times. The data are similar to those discussed in earlier section. For example, there is rise in pH and decrease in final phosphate concentration with an increase of contact time. Figures 4.7 and 4.8 show phosphate removal from acidified solutions, in comparison with normal solutions.

Table 8 shows efficiency of removal and AEC, calculated in case of acidified solutions. Same relationship have been used for these calculations, as described earlier. Once again, efficiency of removal showed its dependence on initial phosphate concentration.

The following general conclusions emerge from the data collected so far:

- (1) There exists a fair correlation between phosphate removal and pH of the solution. A decrease in the final phosphate concentration was always found to be accompanied by a rise of final pH of the solution. This fact apparently indicates replacement of phosphate ions by hydroxyl ions located at the surfaces of clay minerals. This mechanism was proposed by Grim (1953). As quoted by him, there are strong evidences, based on infrared adsorption and deuterium-tagged hydroxyls, which show conclusively that the OH^- ions of clay mineral surfaces can enter into exchange reactions.

- (2) On lowering initial pH of the solution, there was more rapid rise of pH, as well as more rapid and greater removal of phosphate, making the soil more efficient in this aspect.

Presence of iron oxides in the soil is responsible for this fact. As described in Chapter II, surface charge of iron oxides is dependent on relative availability of H^+ and OH^- ions i.e. pH of the solution (Schwertmann and Taylor, 1977). Also, there is a particular pH, called as zero point of charge (ZPC), where equal amounts of H^+ and OH^- ions are adsorbed, making iron oxide particles electrically neutral. Bringing down initial pH of the solution is nothing but an attempt to make iron oxides adsorb more H^+ ions and thus to create more positive sites on the surfaces, by the virtue of which they adsorbed more phosphate.

- (3) In case of normal phosphate solutions, efficiency of removal decreases with an increase in initial phosphate concentration, although initial pH shows a decrease. This fact reveals that initial concentration has a stronger hold over efficiency of removal than initial pH of the solution.

(4) The efficiency values themselves compare well with standard methods of phosphate removal. For example, Sadhukhan and Raymahashey (1972) found that in the alum coagulation method with initial phosphate levels of 4 to 30 mg/l at the optimum pH of 6 and most effective Al : P molar ratio of 2 : 1, the efficiency of removal was 87.5 to 98.0 percent. In the present method, efficiencies achieved at different initial phosphate levels are of the same order as in alum coagulation method, and at low initial phosphate levels even higher than this. Thus efficiency of removal, apart from less cost and easy availability of lateritic soil is a factor, which can make the present technique as suitable as conventional chemical methods.

4.2.3. MECHANISM OF PHOSPHATE REMOVAL:

From the figures 4.7 & 4.8 an equilibrium (constant $P_i - P_F$) seems to be reached after an instantaneous removal of phosphate. This equilibrium can be termed as 'first equilibrium' since it is followed by another equilibrium stage after a certain length of time, which actually is the 'final equilibrium'. The first stage of instantaneous equilibrium can be related to the exchange of phosphate ions with exposed hydroxyl ions at the surfaces of clay minerals and adsorption of phosphate ions on the positive sites of iron oxide surfaces which resulted due to pH of the solution being lower than zero point of charge (ZPC).

Due to presence of intermediate halloysites of different hydration, entrance of dissolved phosphate ions along with water into its interlamellar spacings can not be ruled out. Entry into interlamellar spacings of clay minerals is equivalent to intraparticle transport as concluded for pesticide adsorption by montmorillonite (Huang and Liao, 1970), Weber and Morris (1963) while discussing ABS adsorption on activated carbon had pointed out earlier that a functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with half power of time rather than with time. Therefore, a linear relationship between residual concentration (or removal) and half power of time can be taken to indicate intraparticle (or inter-lamellar) diffusion as the rate-controlling step particularly at the initial stages of removal of a dissolved substance. This was found to be true for dye removal by clays (Sethuraman and Raymahashay, 1975) and for mercury sorption on coal (Pandey and Chaudhuri, 1980).

Figures 4.9 to 4.13 are plots of final phosphate concentration against half power of time for phosphate-soil system under various experimental conditions. Most of them show a sloping linear segment between the instantaneous and final equilibrium stages.

The linear segment is indicative of halloysite playing an equally important role in removal of phosphate along with kaolinite and iron oxides.

Thus in the total process of phosphate removal, four distinct stages can be differentiated:

- (1) Instantaneous removal stage, during which kaolinite and iron oxides play their role,
- (2) First equilibrium stage, which results, when instantaneous removal ceases, but phosphate ions are yet to enter interlayer spacings of halloysites.
- (3) Gradual removal stage, during which dissolved phosphates make their entry into interlayer spacings of halloysites, and
- (4) Second and final equilibrium stage, where gradual removal also ceases.

Acidification of the initial phosphate solutions in the range 2 to 25 mg/l caused appearance of curved segments in the plots of final phosphate concentration versus square root of time (Fig.4.10 to 4.12). Appearance of these curved segments displaced the first equilibrium stage to a longer contact time. This feature was apparently due to the increased adsorption on iron oxides in lower pH range. Acidification caused an increase in the ratio of $\text{OH}_2^+/\text{OH}^-$ surface groups. It created more positive sites on iron oxides surfaces, as a consequence of which they adsorbed more phosphate

(Bowden et al., 1974). The curved nature of the kinetic graph also suggests that the rate of adsorption was not constant but gradually decreased with time.

In case of very low initial concentration (2 mg/l), curved segments appeared in normal as well as acidified solution, and this was followed by final equilibrium. The third gradual removal stage did not appear at all (Fig.4.9). This phenomenon can be attributed to the instantaneous removal stage of kaolinite and iron oxides, which cause complete removal of phosphate.

A completely contrasting feature developed in case of solution of 50 mg/l initial phosphate concentration, in which curved segment did not appear, even on acidification (Fig.4.13). Here apparently, due to relatively high concentration, instantaneous removal was completed before 3 hours.

An increase in the slope of linear segments with initial phosphate concentration indicated that rate of gradual phosphate removal by halloysites increased with initial concentration (Fig.4.14 and 4.15).

For low initial phosphate concentration, desorption of phosphate i.e. a temporary increase in residual concentration was also observed (Table 2 and figures 4.7 & 4.9). This phenomenon has been observed by many workers, as quoted by Orme and Nelson (1979). The desorbed phosphate was apparently physically-bounded, which came out due to concentration difference between equilibrium solution and the soil.

Fig.4.16 is an adsorption isotherm which has been extrapolated towards equilibrium, because the data collected were not sufficient to plot a complete isotherm. In this context it can be mentioned that previous work indicates that equilibrium values in similar isotherm plots come at very high phosphate concentrations, of the order of 250 mg/l (Orme and Nelson, 1979). Such high phosphate concentrations are beyond the scope of the present work, being unusual in natural waters as well as in industrial and domestic wastes.

4.3. PHOSPHATE UPTAKE BY VARKALA LATERITIC SOIL:

To study phosphate uptake by Varkala lateritic soil, first 0.5 g of soil was kept in contact of 50 cc of phosphate solution of 2 mg/l initial concentration and later on soil amount was increased to 1.0 g, since in the former case, phosphate uptake by the soil was found to be relatively very poor.

4.3.1. UPTAKE FROM NORMAL SOLUTIONS:

Data related with phosphate uptake by 0.5 g of soil is presented in table 9 and Fig.4.17 shows these graphically. Again, in this system also, a continuous rise of pH was observed till the equilibrium was reached. In between 6 and 18 hours, phosphate was removed slowly. Then an increase in the rate of phosphate removal (Fig.4.17) indicated introduction of some new site for phosphate uptake, completing the process at 21 hours and bringing the system ^{to} equilibrium.

Amount of phosphate uptake was 1.65 mg/l out of 2 mg/l, efficiency of removal (e) as defined earlier being 82.5%.

4.3.2. UPTAKE FROM ACIDIFIED SOLUTIONS:

Fig.4.17 and data of table 9 show that acidification of the initial solution did not improve the situation much as far as uptake capacity of the soil was concerned. In the present system, 1.7 mg/l phosphate was removed (efficiency = 85 %). This time a new site for uptake did not appear during the process. Equilibrium reached in 30 hours; 6 hours later than that observed in case of normal solution, which apparently was due to slightly more phosphate uptake.

Fig.4.18 is a plot of final phosphate concentration versus square root of contact time, implications behind it being same, as discussed in earlier sections. In case of normal solutions, curved segment is followed by a linear one, before equilibrium is reached, again an indication of two sites of uptake. The first site was surfaces of clay minerals and iron oxides, and second site was interlayer spacing of halloysites, giving a linear segment in the plot. In case of acidified solution, this linear segment disappeared, which indicated that the whole phosphate removal was due to adsorption on surfaces of clay minerals and iron oxides.

The very low efficiency of phosphate removal of Varkala soil even after acidification was apparently due to its very low iron oxides content and high proportion of Quartz and feldspar, which do not contribute in phosphate uptake.

Here also, desorption of phosphate was observed (Fig.4.17) which is characteristic of low initial phosphate levels.

4.3.3. EFFECT OF HIGHER SOIL PROPORTION:

One run with higher soil proportion was undertaken to increase the efficiency of Varkala soil, if possible. With double soil proportion (1.0 gm in 50 cc solution) it was found that removal was 100 percent from the acidified solution of initial level of 2 mg/l (Fig.4.17).

This was obviously due to higher amounts of clays and iron oxides, in contact ^{with} / the phosphate in solution. This experiment suggests that phosphate uptake, in general, would increase with higher soil to solution ratio.

4.3.4. UPTAKE DIFFERENCES OF CALICUT AND VARKALA SOILS:

Comparative studies of performances of the Calicut and the Varkala soils reveal that former is far better suited for phosphate uptake than the latter. Efficiency of Varkala soil for phosphate uptake is only 85% at 2 mg/l initial level, whereas that of Calicut soil is 100% at that level and falls to 98% at an initial level of 50 mg/l.

These differences can be attributed to the mineralogical differences of the two soils, which in turn were due to differences of parent rocks.

In case of Calicut soil, quartz was the only mineral constituent, which did not have any contribution in phosphate uptake. However, very high proportion of iron oxides in this soil, not only neutralised this factor, but at the same time made the soil very efficient in phosphate uptake. On the other hand, presence of abundant Quartz and feldspar (the second mineral constituent of the soil, having no contribution in phosphate uptake) and negligible amounts of iron oxides made the Varkala soil comparatively inefficient for the phosphate uptake.

4.4. ELECTROPHORESIS EXPERIMENT:

From the forgoing discussions, existence of positive charge over iron oxides present in the lateritic soils is beyond any doubt. At this stage, the only technique which could give a clear cut idea of nature of charge over clay particles and iron oxides was Electrophoresis.

Electrophoresis, or cataphoresis is the movement of particles, including colloid particles, drops, globules and bubbles in an induced electric field (Yariv and Cross, 1979). They quote that ferric hydroxides are positively charged as during a U-tube experiment, brown colour of this substance was

seen to move towards the cathode during electrophoresis. On the other hand, Van Olphen (1963) cites evidence in support of the fact that clay particles are negatively charged.

In the present work, during the electrophoresis of the two lateritic soils, no movement, and subsequently no deposition of soil components occurred on either of the electrodes. An increase in the duration of current flow did not make any difference. However, repeating the same experiment with kaolinite (an iron oxide free material), deposition occurred on the anode. This experiment thus confirmed a net negative charge on clay particles. No deposition of kaolinite particles on anode without flowage of current, further confirmed the earlier deposition to be of electrophoretic nature. However, in the lateritic soils the negative charge on the clay particles was neutralised by the positive charge on iron oxides. This result, thus, indirectly proves the presence of positively charged iron oxide particles in a lateritic soil.

4.5. PHOSPHATE UPTAKE BY COMMERCIAL KAOLINITE:

In order to properly evaluate the effects of iron oxides of lateritic soils on phosphate uptake, a comparison of their performance with an iron oxides free material was thought to be of considerable importance. The major reason for choosing kaolinite as iron oxide free material for subsequent experiments was its presence in lateritic soils, together

with iron oxides. Thus, it would lead to direct conclusions, as far as the effect of the presence of iron oxides was concerned.

4.5.1. IMPURITIES IN SAMPLE:

X-ray analysis of commercial kaolinite sample reflected the presence of a small proportion of halloysite, illite and quartz in addition to kaolinite as the main mineral. Relative intensities of the peaks led to the conclusion that among these impurities quartz was the dominant, whereas the other two were present in very less amounts (Fig.4.19).

4.5.2. UPTAKE FROM NORMAL SOLUTIONS:

Amounts of phosphate removed, final phosphate concentration, and pH value of the solutions at different times are shown in tables 10 to 14. The results are graphically shown in figures 4.20 & 4.21. A critical inspection of the changes in pH values of the solutions and amount of phosphate removed at a particular time again supported the mechanism of phosphate uptake, involving exchange of hydroxyl ions with phosphate ions.

Equilibrium was reached in every case in 18 hours. Kaolinite removed phosphate completely from solutions of initial concentrations of 2 and 5 mg/l. However from the solutions of 10, 25 and 50 mg/l concentration, removal was only 82, 70 and 58 percent respectively (Table 15).

On plotting the final phosphate concentrations versus square root of time, only a curved segment appeared before equilibrium (Figures 4.22 to 4.26). This was because uptake of phosphate was restricted to the surfaces and edges of kaolinite particles and rate of removal decreased with time. Halloysite, present as an impurity in the sample, obviously was not in sufficient amounts to cause a change in the uptake mechanism.

4.5.3. UPTAKE FROM ACIDIFIED SOLUTIONS:

Acidification caused a slightly more rapid changes in the final pH values of the solutions than that observed in case of normal solutions (Tables 10 to 14). Also, from the acidified solutions, removal of phosphate was higher. From the solutions of 2 and 5 mg/l initial phosphate levels, removal once again was complete (Fig. 4.20), whereas from the solutions of 10, 25 and 50 mg/l initial levels, removal was 90, 76 and 62 percent, (Fig. 4.21). An increase in the uptake capacity of kaolinite on acidification of solutions was probably due to destruction of negative sites and occupation of those sites by Hydrogen ions, as a consequence of which net positive charge on the surfaces of kaolinite particles increased (Yariv and Cross, 1979). Efficiencies of removal for different initial phosphate concentrations are shown in Table 16.

Another notable difference observed between phosphate uptake from normal and acidified solutions was the equilibration time. For acidified 2 and 5 mg/l PO_4 solutions, equilibrium was reached in 6 hours, compared to 18 hours for normal solutions and rate of removal was faster in the acidified solution. Equilibrium time, however, remained same for higher phosphate levels (Fig.4.21), although final removal was more in the acidified solutions.

Plots of final phosphate concentration against square root of time showed a curved segment, before equilibrium, similar to normal solutions (Figures 4.22 to 4.26). However, phosphate left in the solutions was lesser, due to an increase in the positive charge of Kaolinite particles.

1.5.4. LATERITES VERSUS KAOLINITE:

Fig.4.27 is a synthesis of data on phosphate removal from acidified solutions by Calicut laterite compared with commercial kaolinite. It is obvious that the pattern of removal depends on the initial phosphate level. For example, with 10 mg/l phosphate, Calicut laterite removes larger amounts than Kaolinite from initial to final stage. For 25 mg/l phosphate, removal is practically the same upto 3 hours and Calicut laterite is more efficient with longer contact time. Moreover, the effect of inter-lamellar removal by halloysite is observed after 24 hours. For 50 mg/l phosphate,

kaolinite is more efficient in the initial stages but the equilibrium limit is reached after 18 hours. On the other hand, after this contact period, inter-lameller removal by halloysite in Calicut laterite rapidly makes up for its initial low efficiency and the final removal is much higher than kaolinite.

These differences between laterite and kaolinite must be due to the relative importance of (i) phosphate removal by positive sites on clays and iron oxides and (ii) phosphate removal by interlameller diffusion in halloysite. It appears that at relatively low phosphate levels, the effect of the first type of removal is more in laterites which contain iron oxides along with clays. However, at higher phosphate levels, the rate of removal by positive sites on kaolinite alone is faster than that on the mineral mixture in laterite. But the halloysite effect in laterite finally removes much more phosphate compared to kaolinite.

The importance of the proportion of iron oxide and clays in lateritic soil in phosphate removal is also clear on comparing these results with the performance of the Varkala Soil (Table 9). This soil with lower clay fraction and iron oxide removed less phosphate than kaolinite even at a low initial level of 2 mg/l in normal as well as acidified solution.

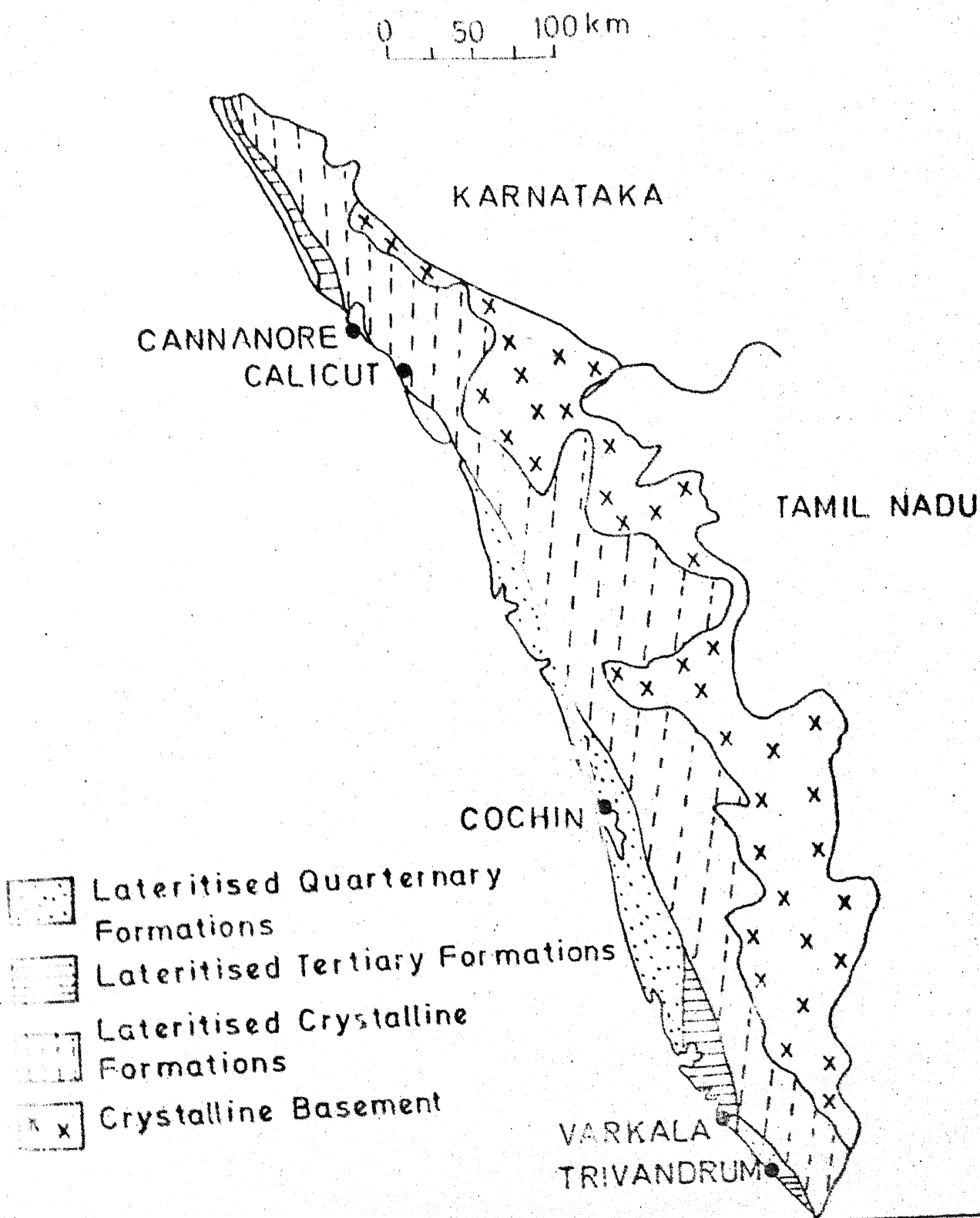


fig. 4.1 - Geological Map of Kerala Showing Outcrops of Laterites.
(Mallikarjuna et al, 1979)

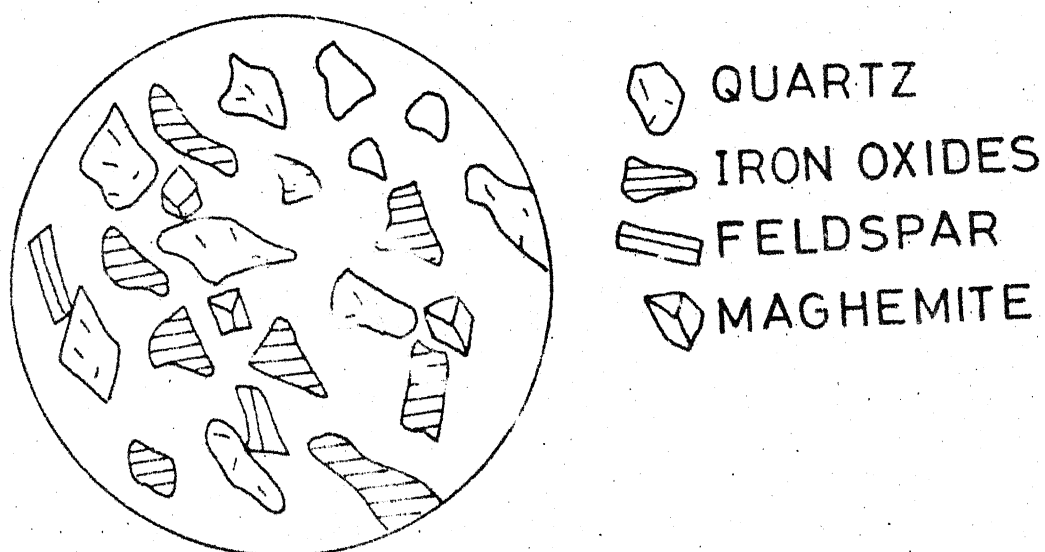
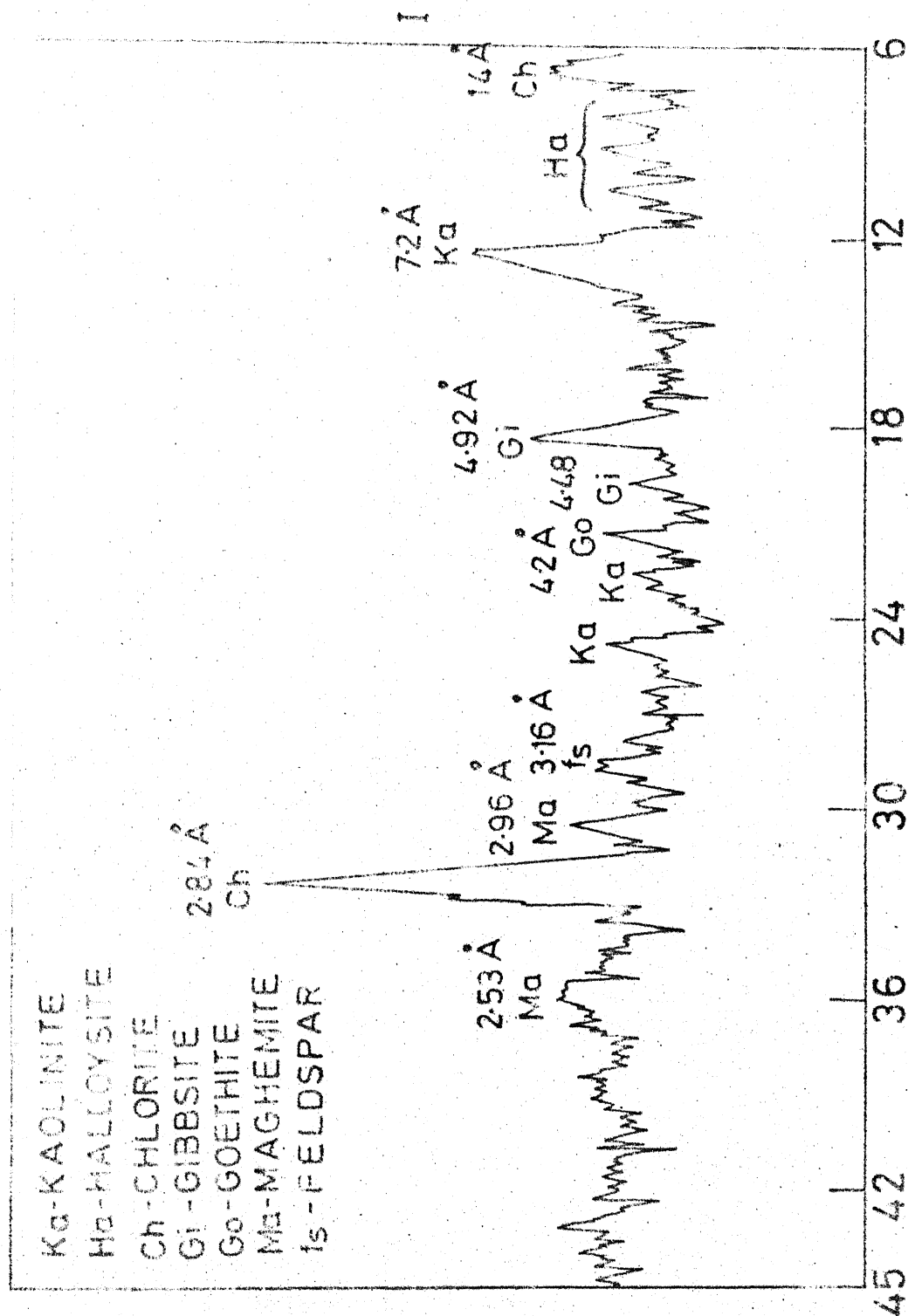


Fig. 4.2 - Sketch of Microscopic View of Coarser Fraction of Calicut Soil after Acid Washing.



2θ (degrees) in Cu radiation

Fig. 4.3 - Sketch of X-ray Diffraction Pattern of Calicut Soil.

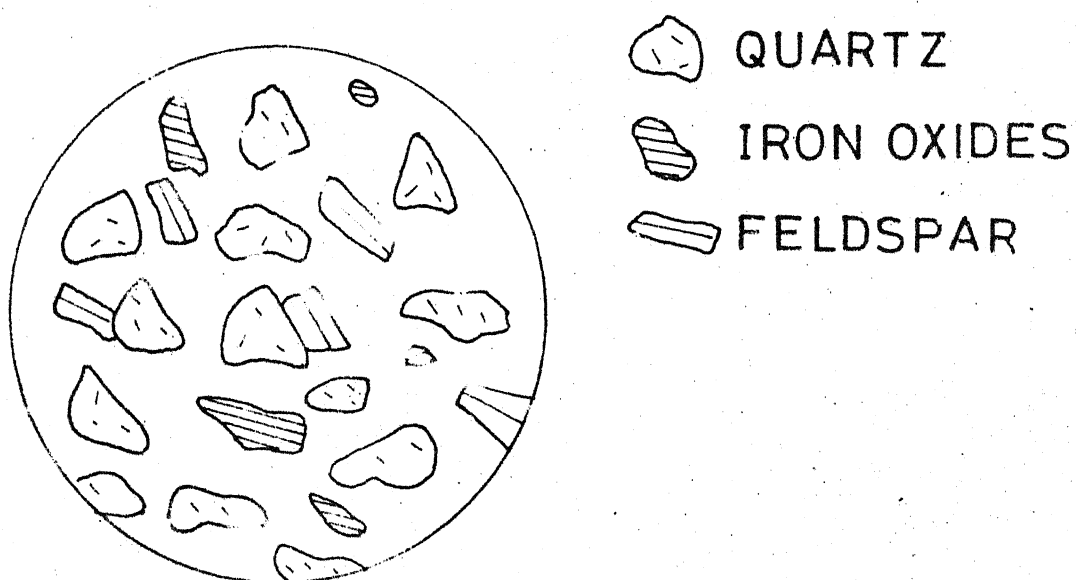


Fig. 4.4.- Sketch of Microscopic View of Coarser Fraction of Varkala Soil after Acid Washing.

CENTRAL LIBRARY
Acc. No. A 82457

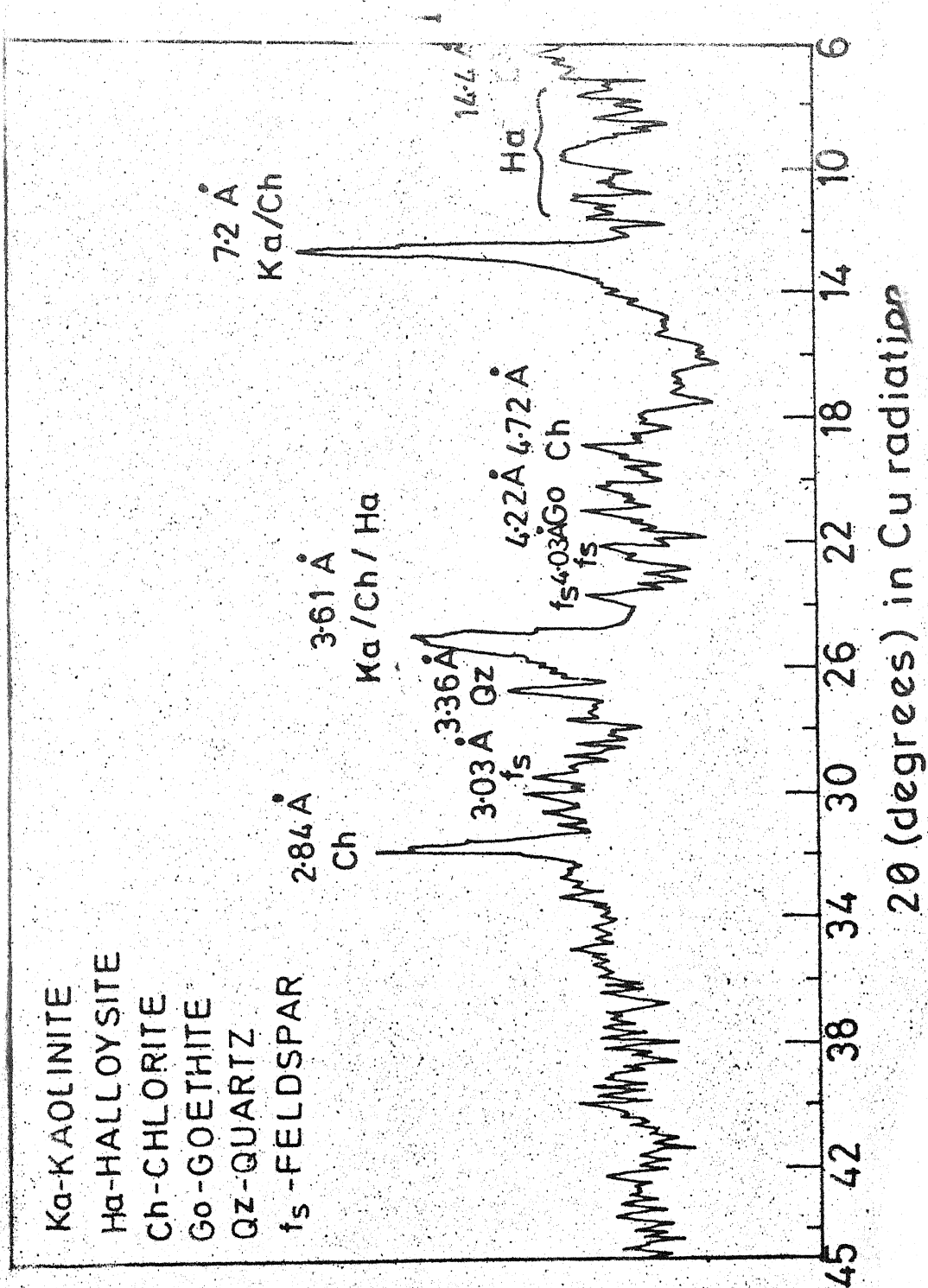


Fig. 4.5 - Sketch of X-ray Diffraction Pattern of Varkala Soil.

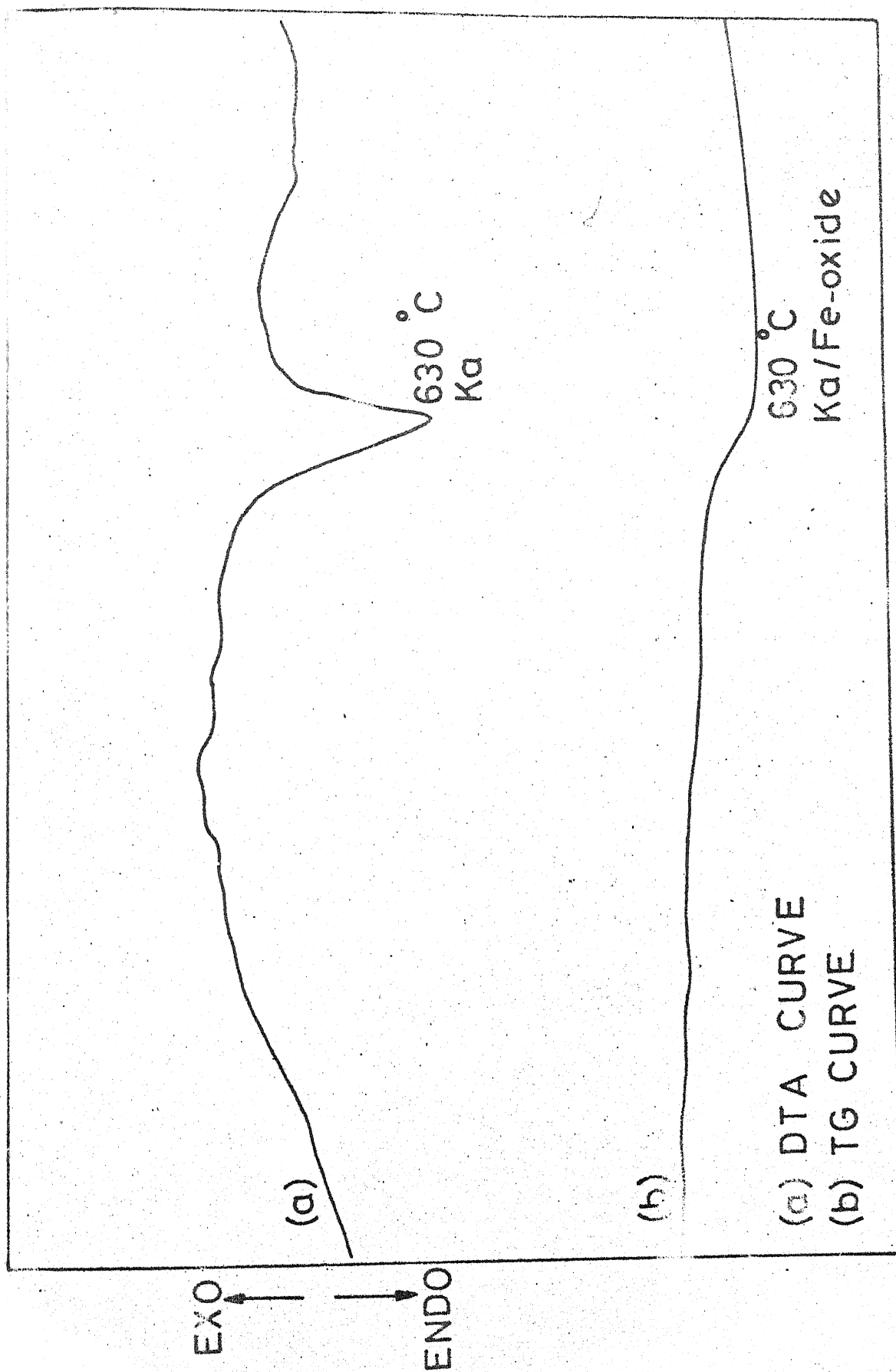


Fig. 4.6 - DTA and TG Patterns of Varkala Soil.

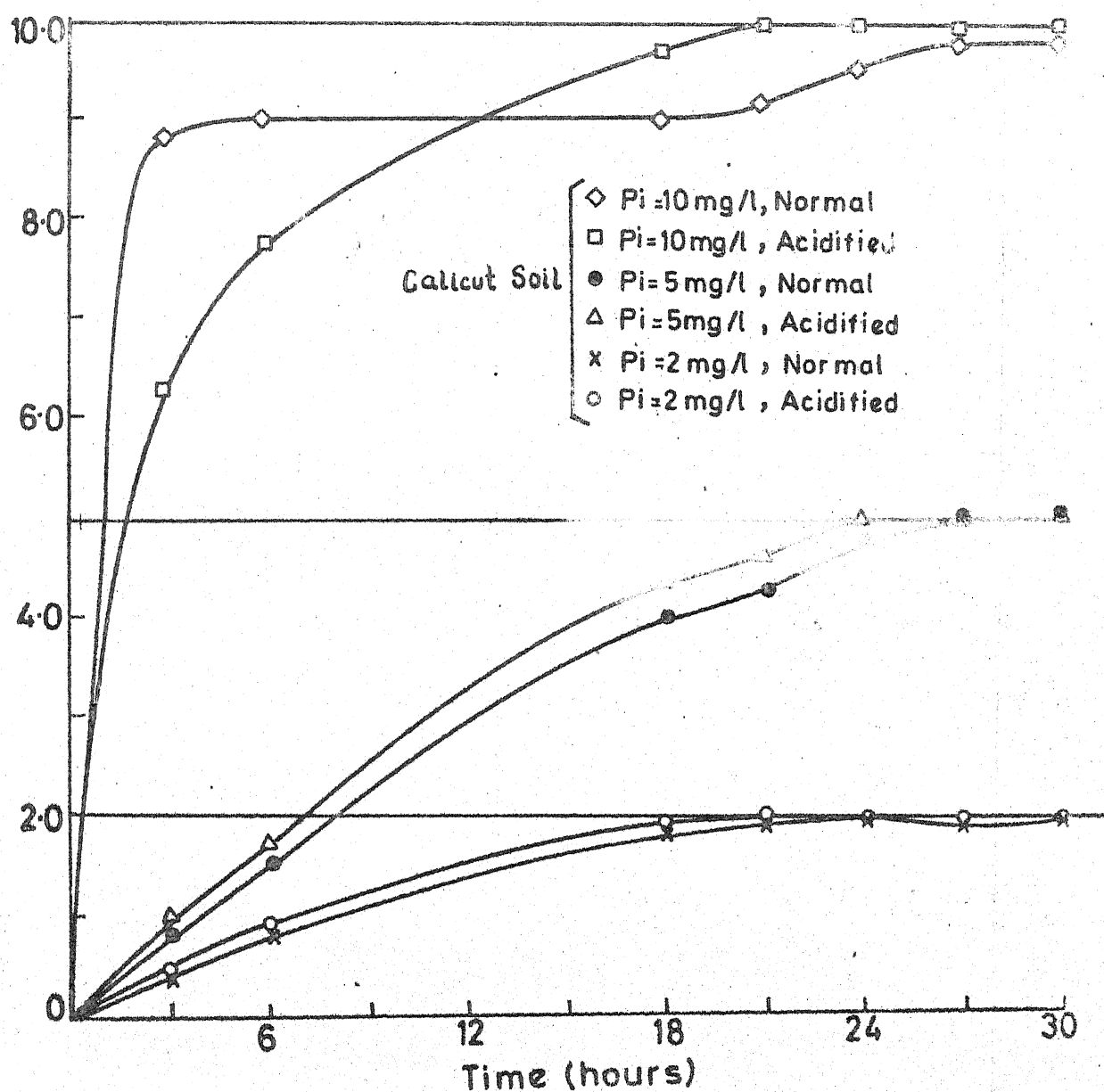


Fig. 4.7 - Phosphate Uptake by Calicut Soil.

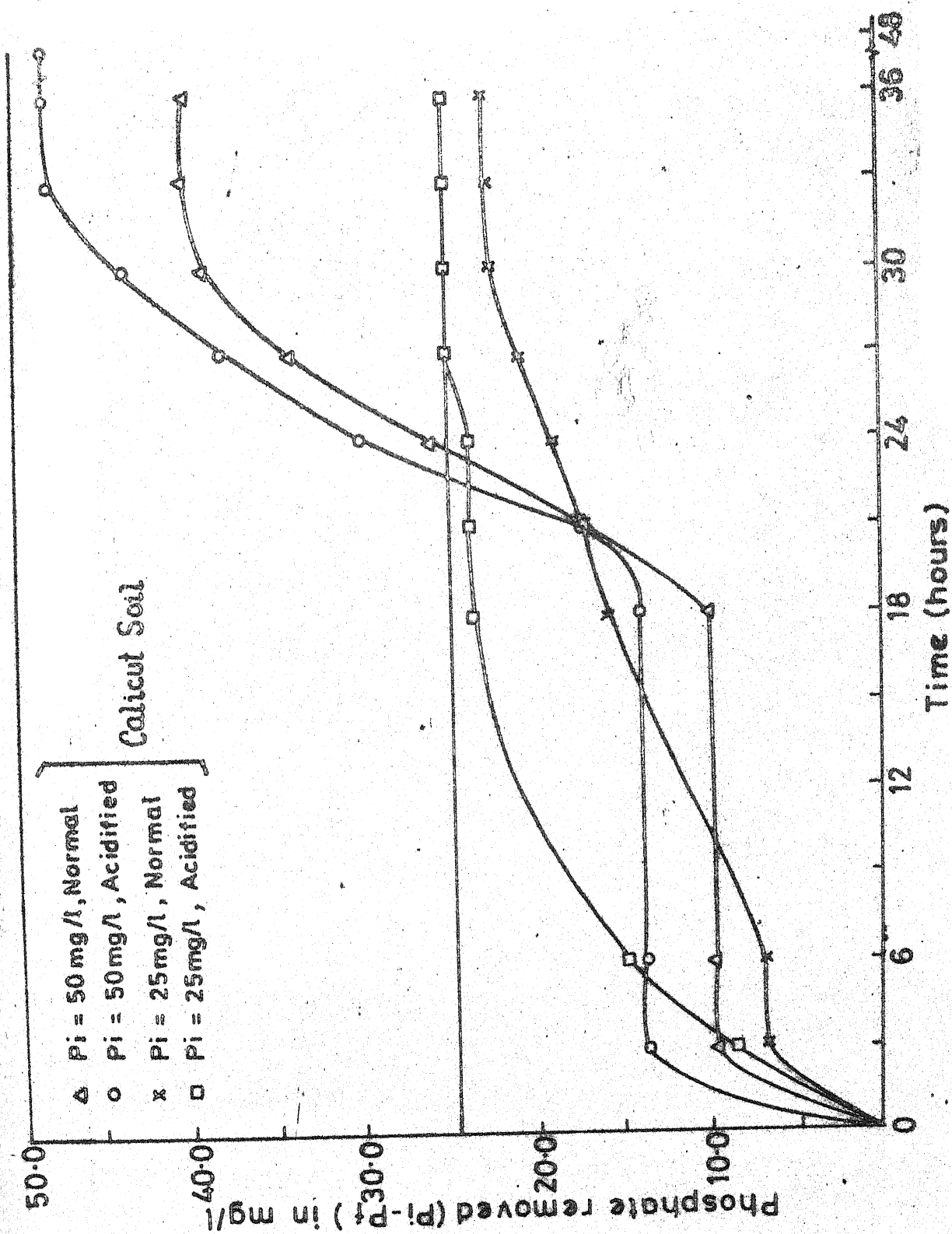


Fig. 4.8 - Phosphate Uptake by Calicut Soil.

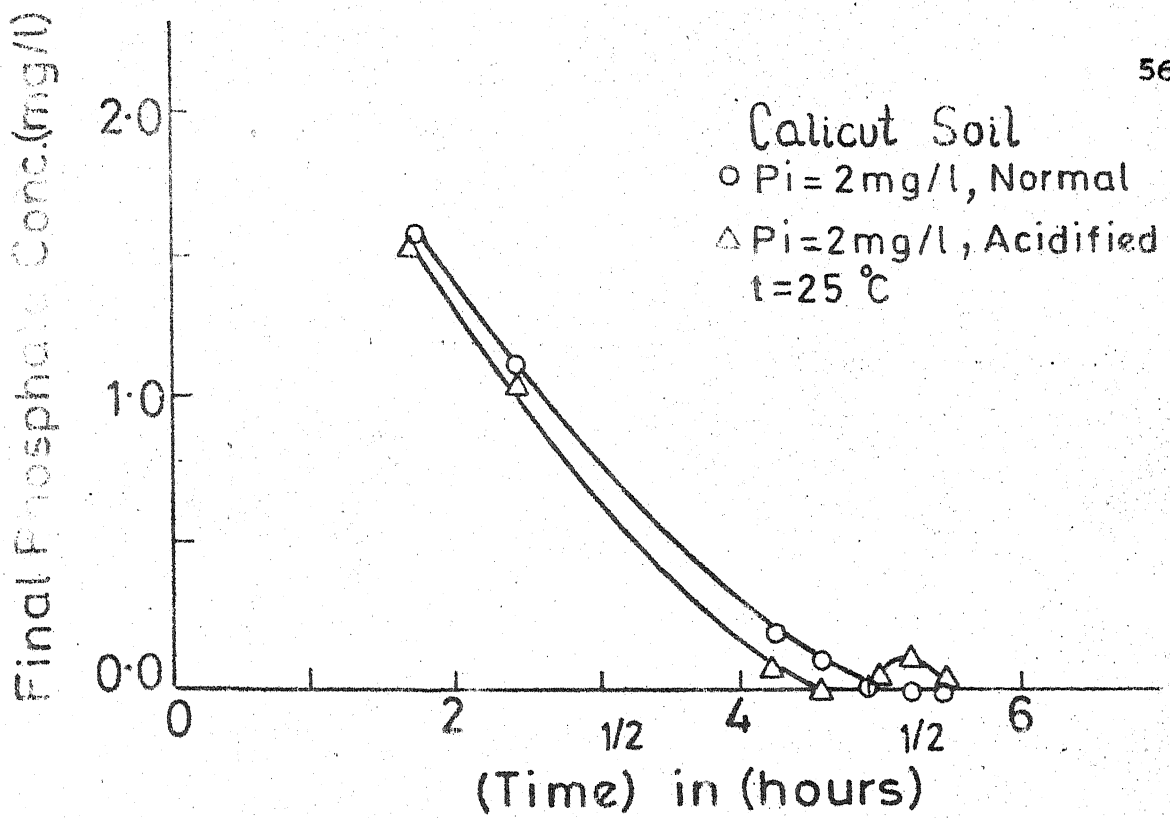


Fig. 4.9 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

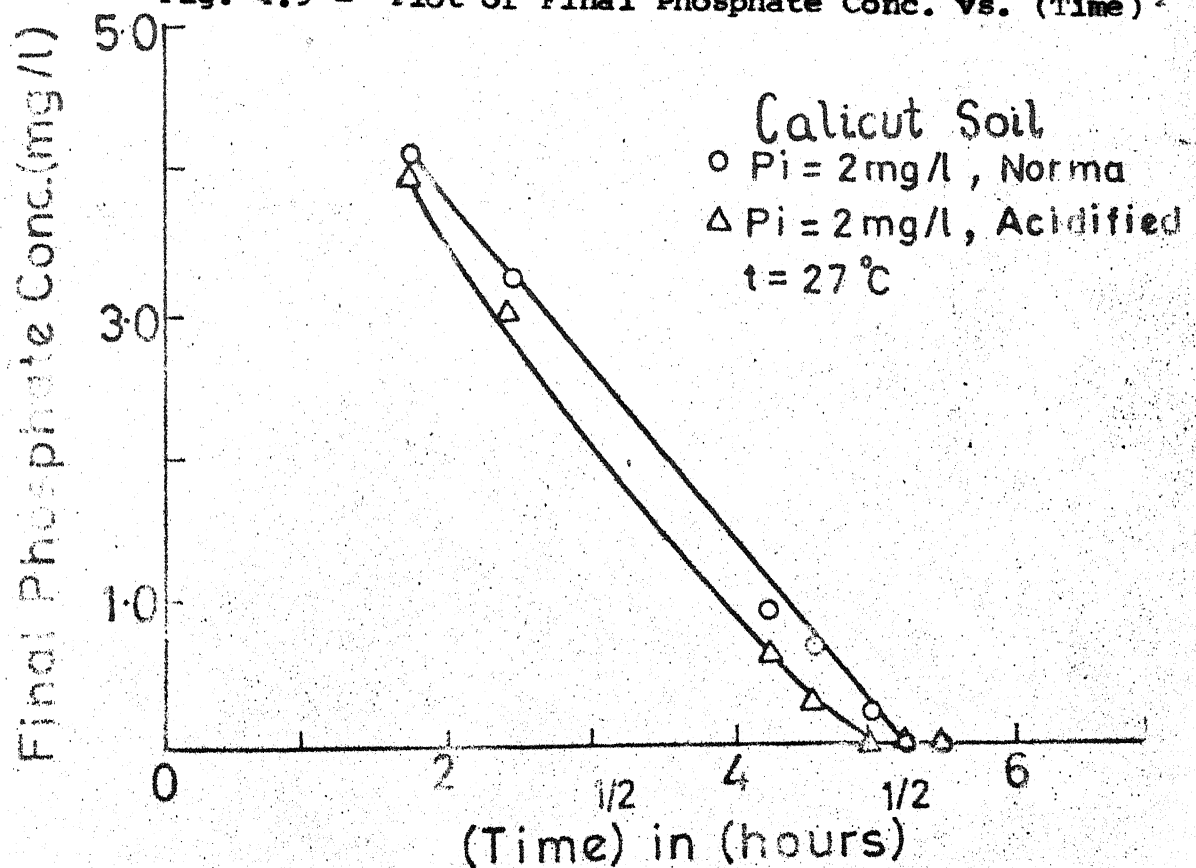
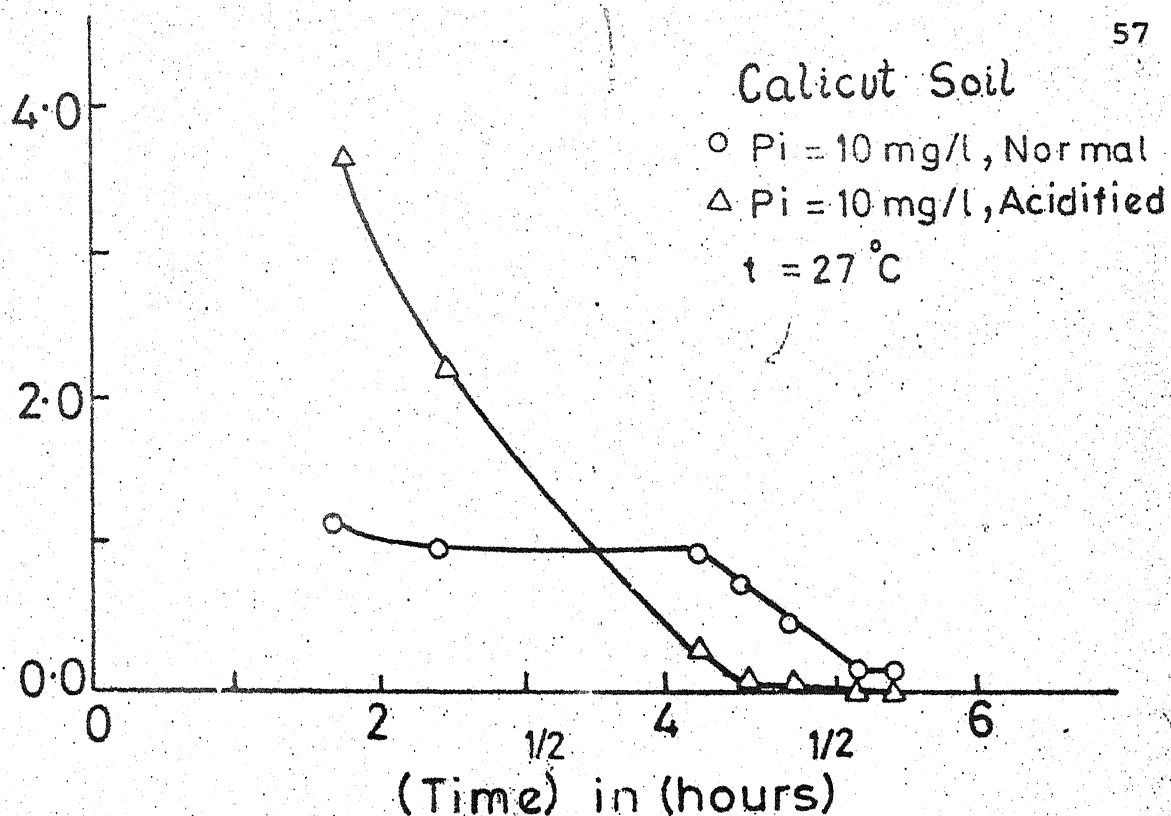
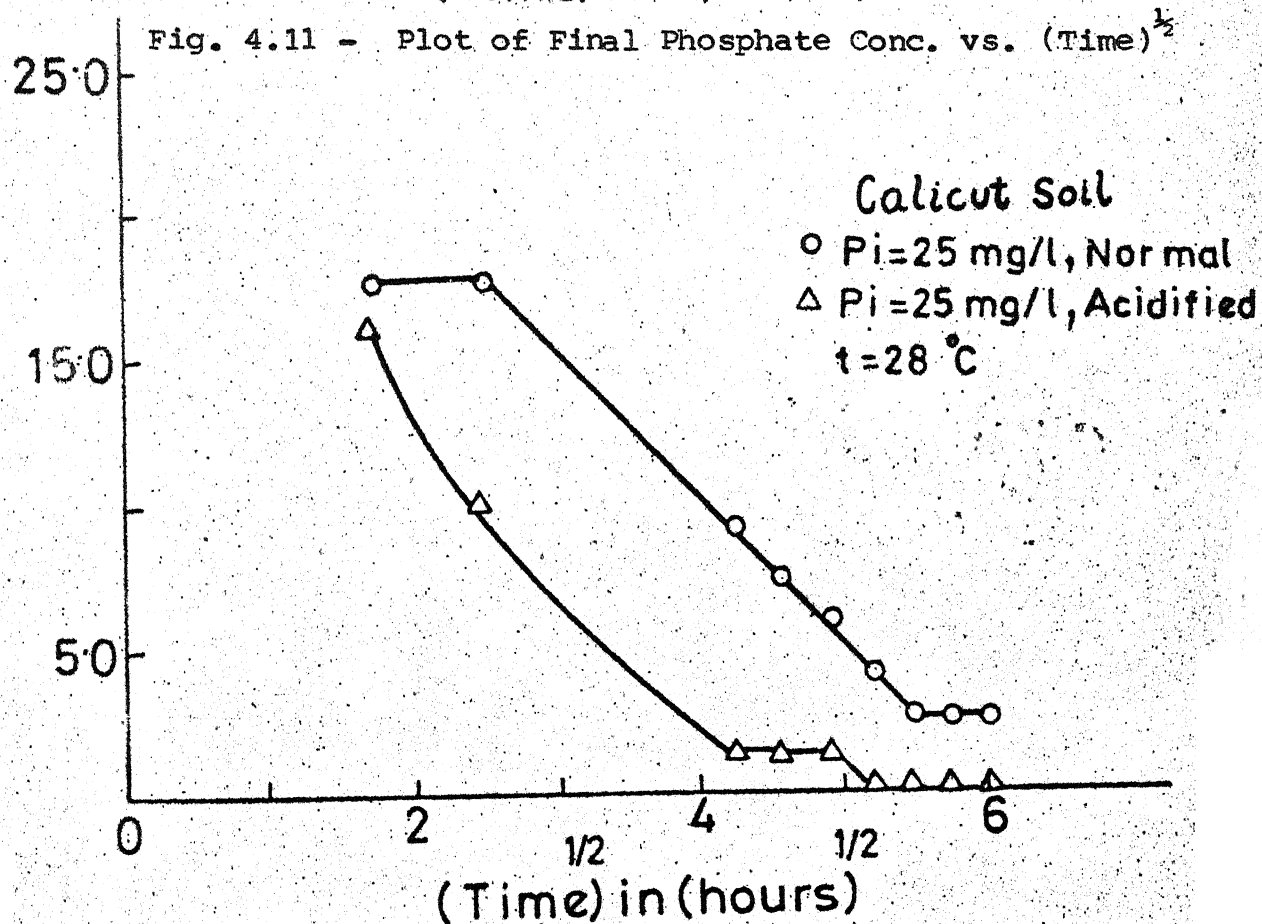


Fig. 4.10 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

Final Phosphate Conc.(mg/l)

Fig. 4.11 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

Final Phosphate Conc. (mg/l)

Fig. 4.12 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

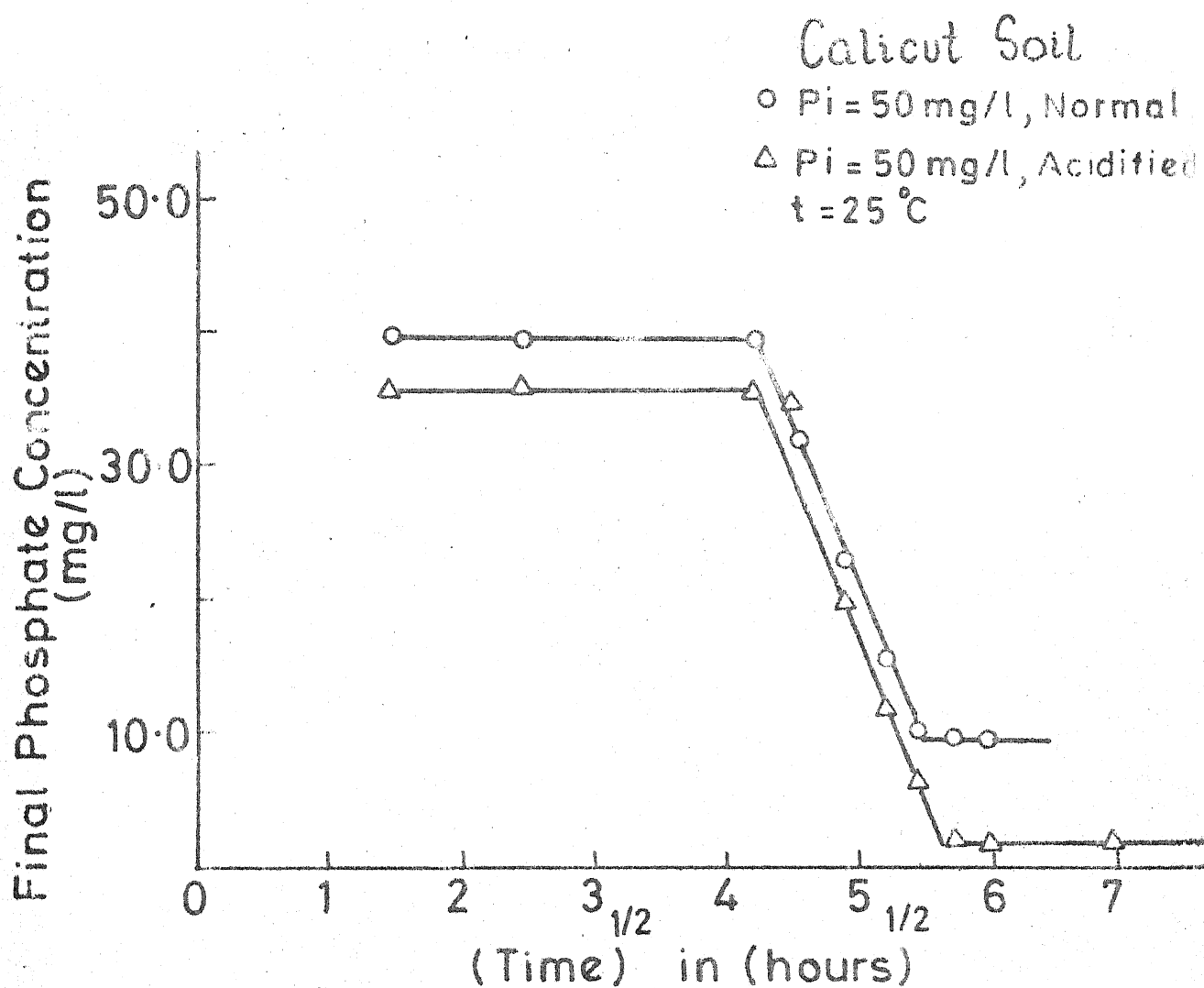


Fig. 4.13 - Plot of Final Phosphate Conc. vs. (Time)^{1/2}

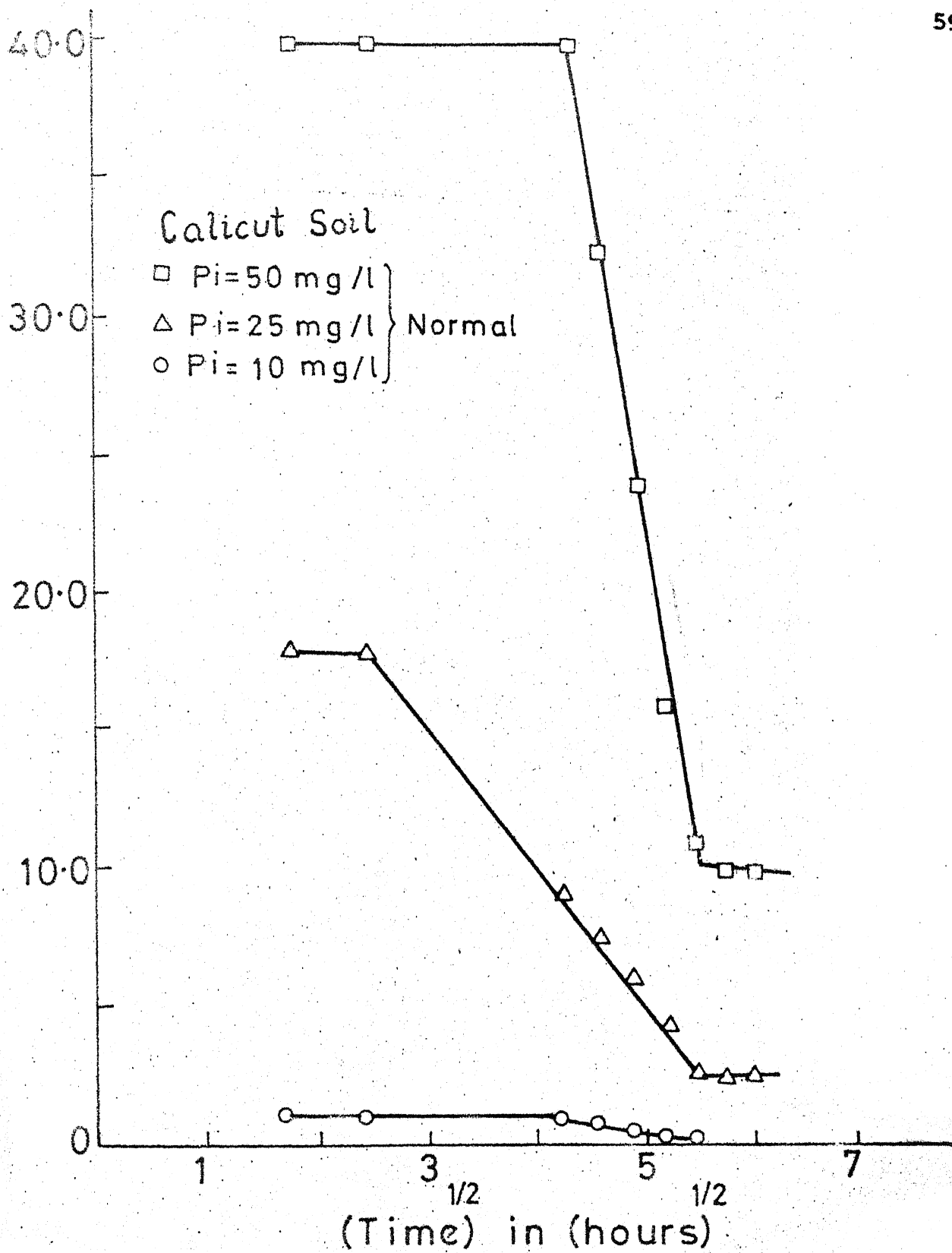


Fig. 4.14 - Plot of Final Phosphate Conc. vs. (Time)^{1/2}

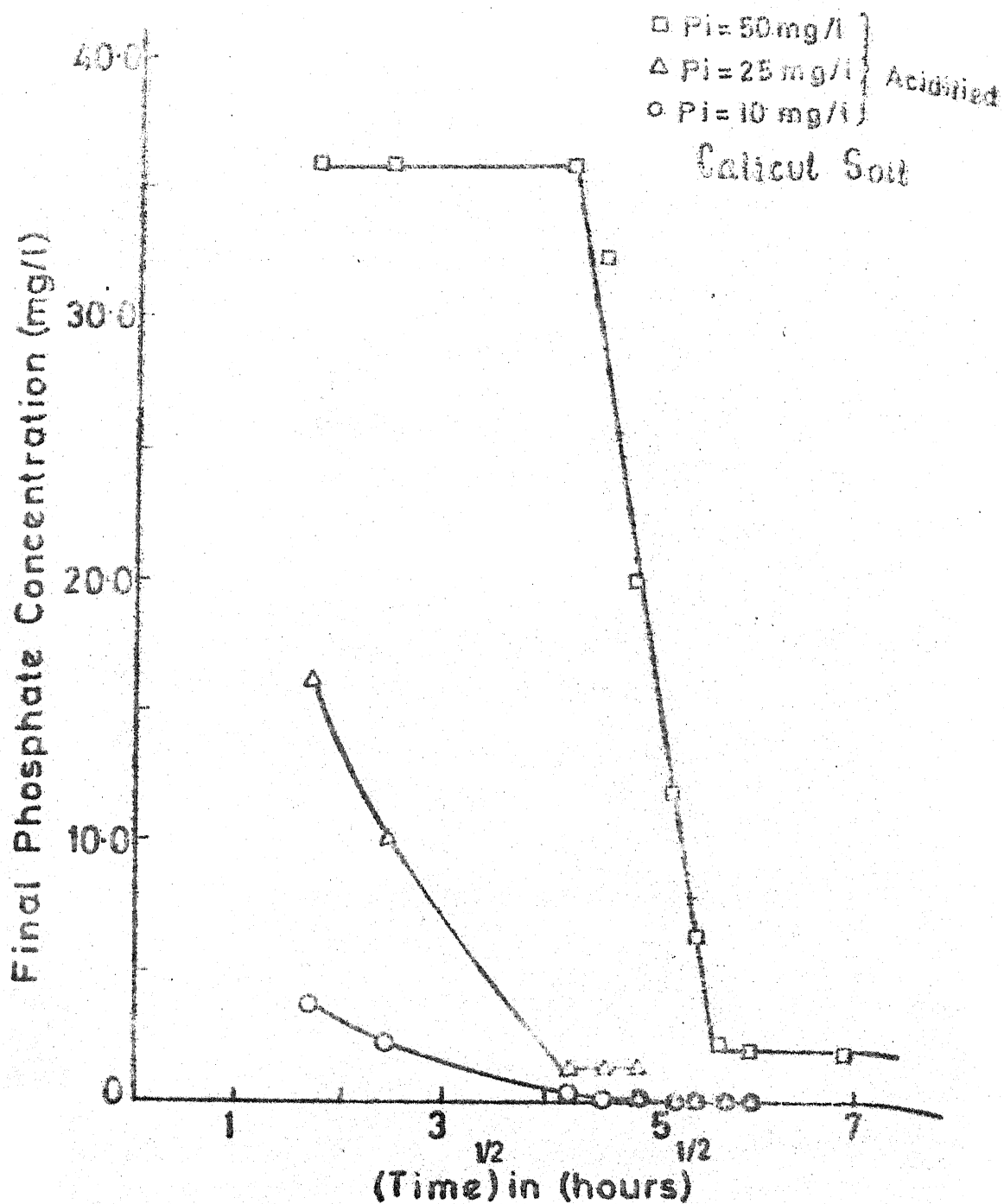


Fig. 4.15 - Plot of Final Phosphate Conc. vs. (Time)^{1/2}

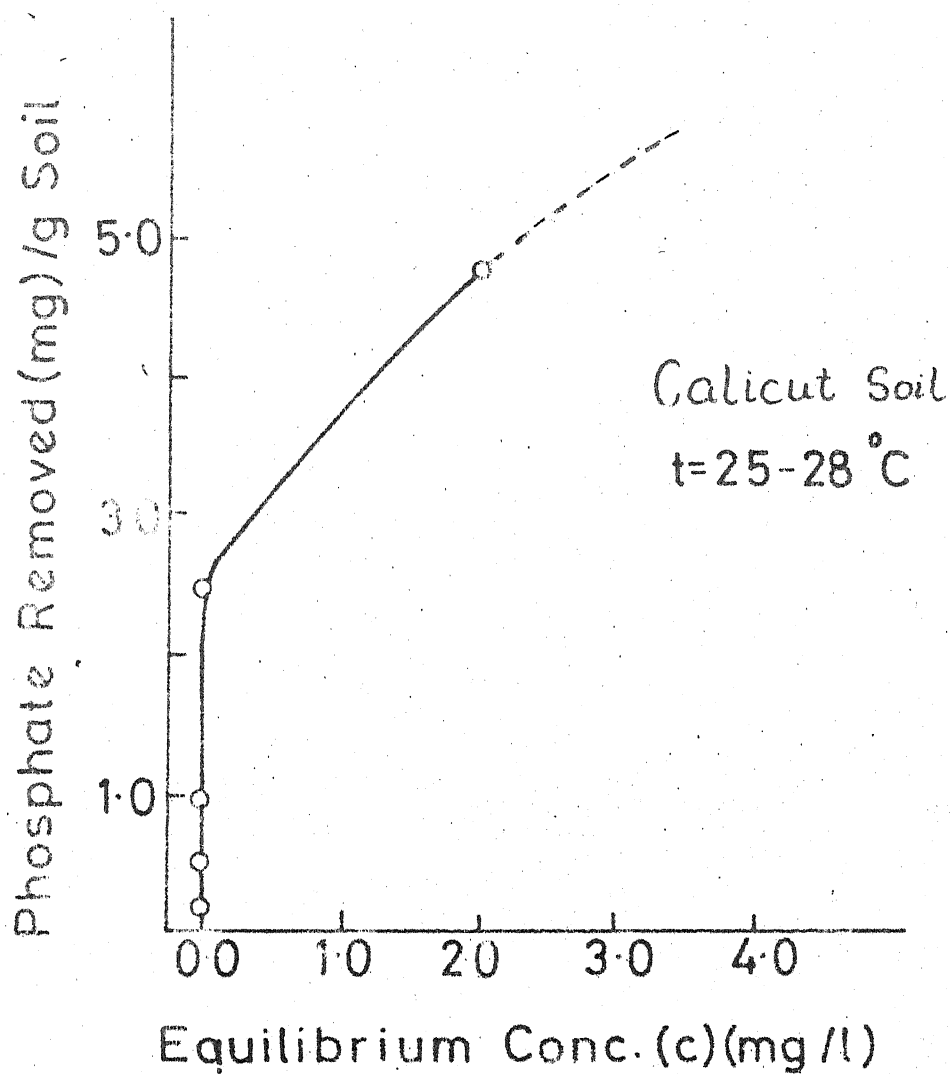


Fig. 4.16 - Extrapolated Adsorption Isotherm.

Varkala Soil
 ○ $P_i = 2 \text{ mg/l}$, normal
 △ $P_i = 2 \text{ mg/l}$, acidified
 □ Higher soil proportion

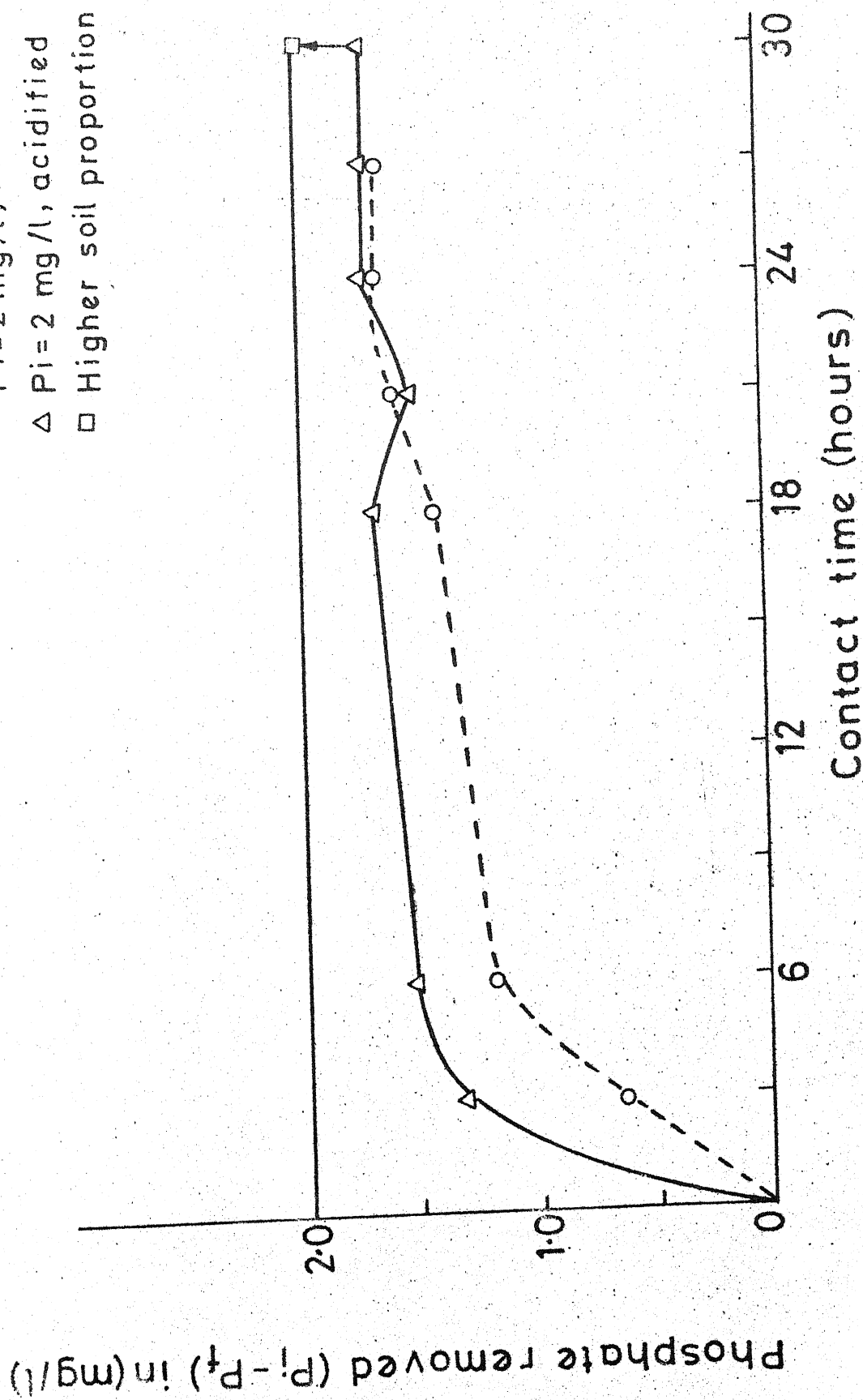


Fig. 4.17 - Phosphate Uptake by Varkala Soil.

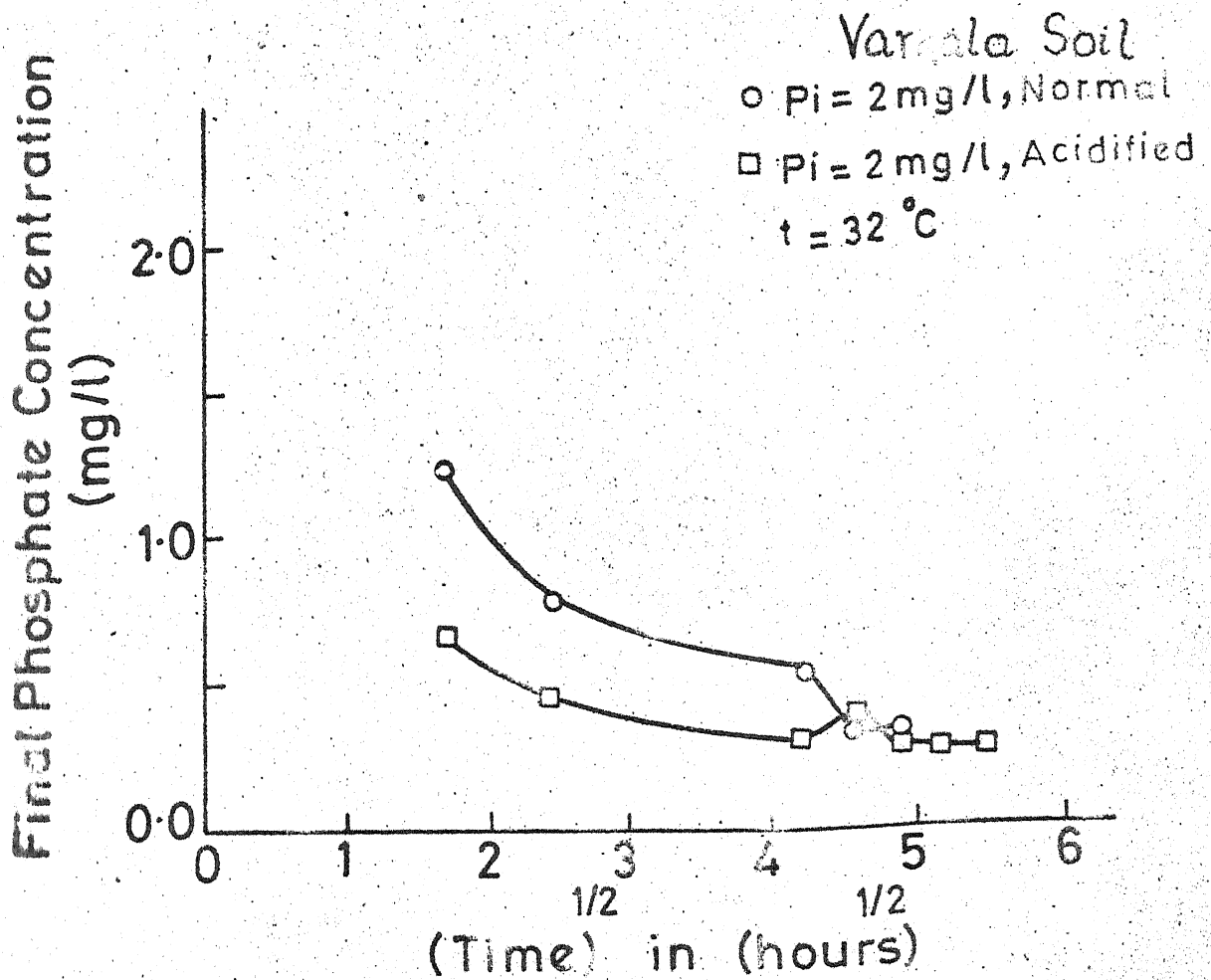


Fig. 4.18 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

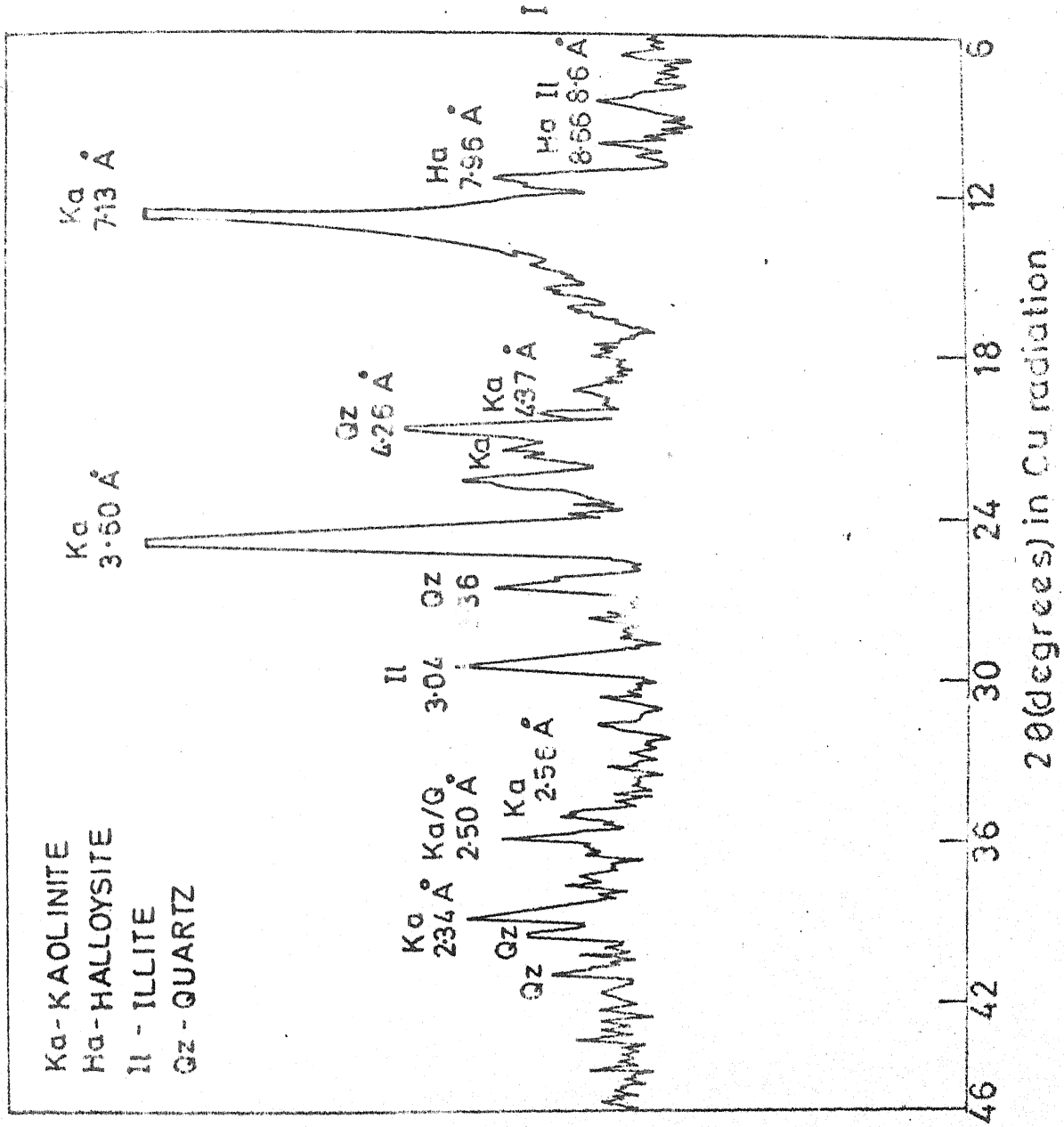


Fig. 4.19 - Sketch of X-ray Diffraction Pattern of Commercial Kaolinite.

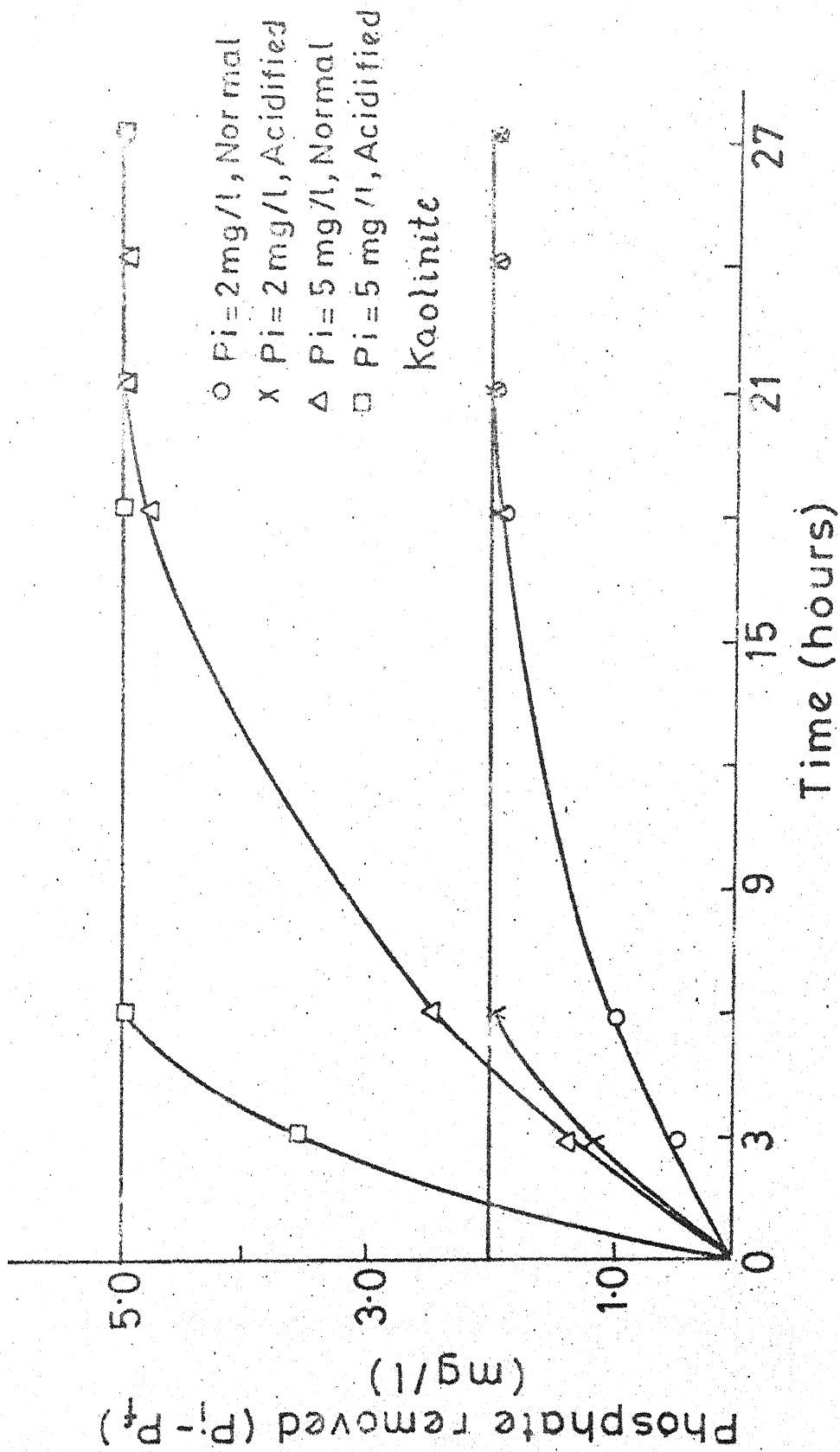


Fig. 4.20 - Phosphate Uptake by Commercial Kaolinite.

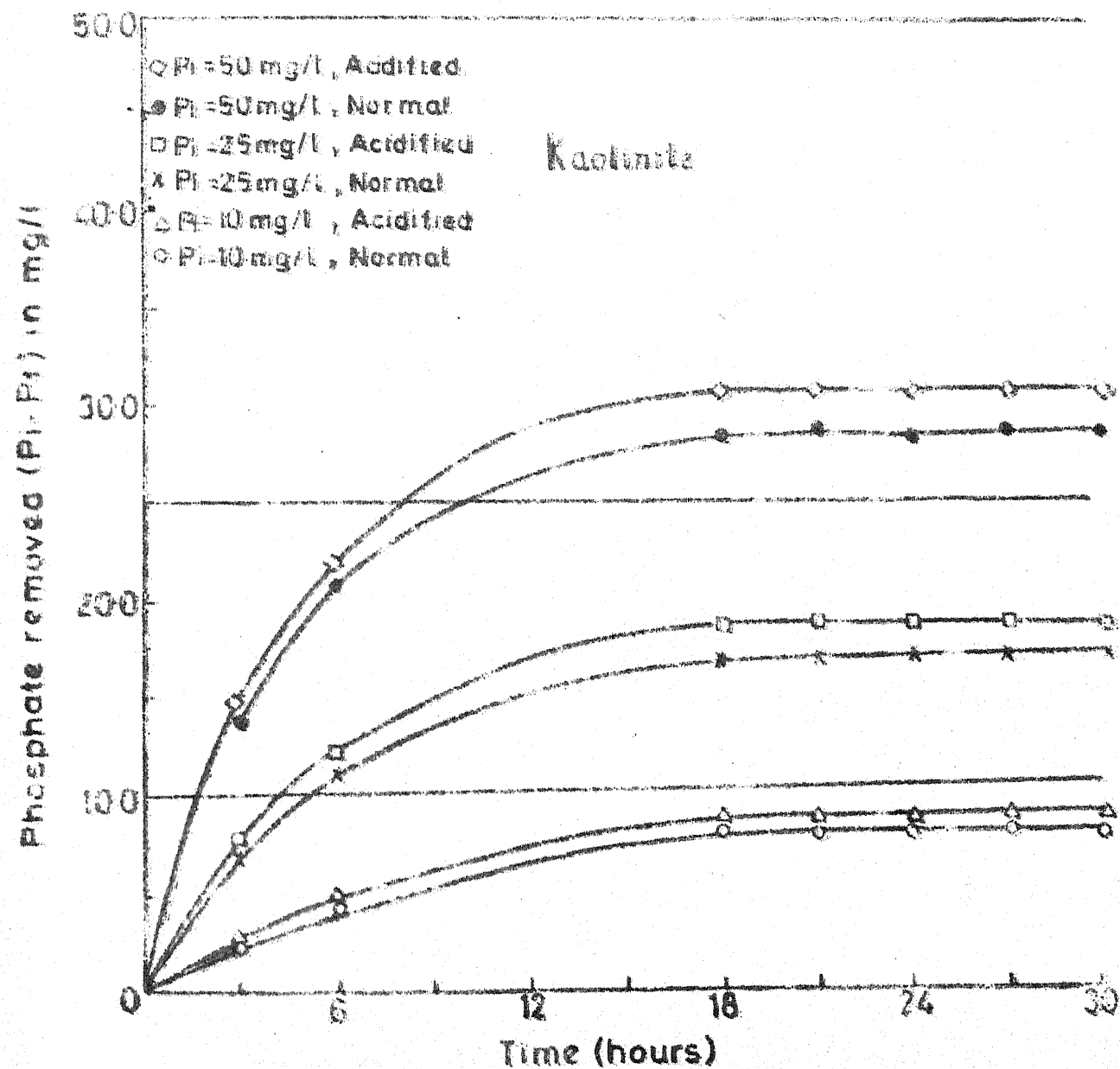


Fig. 4.21 - Phosphate Uptake by Commercial Kaolinite.

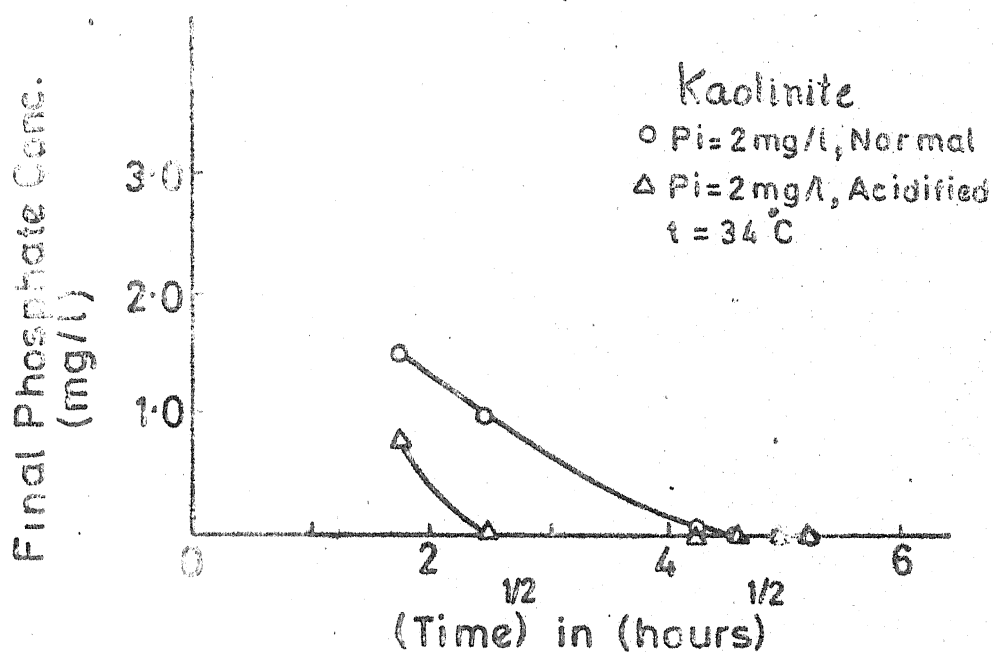


Fig. 4.22 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

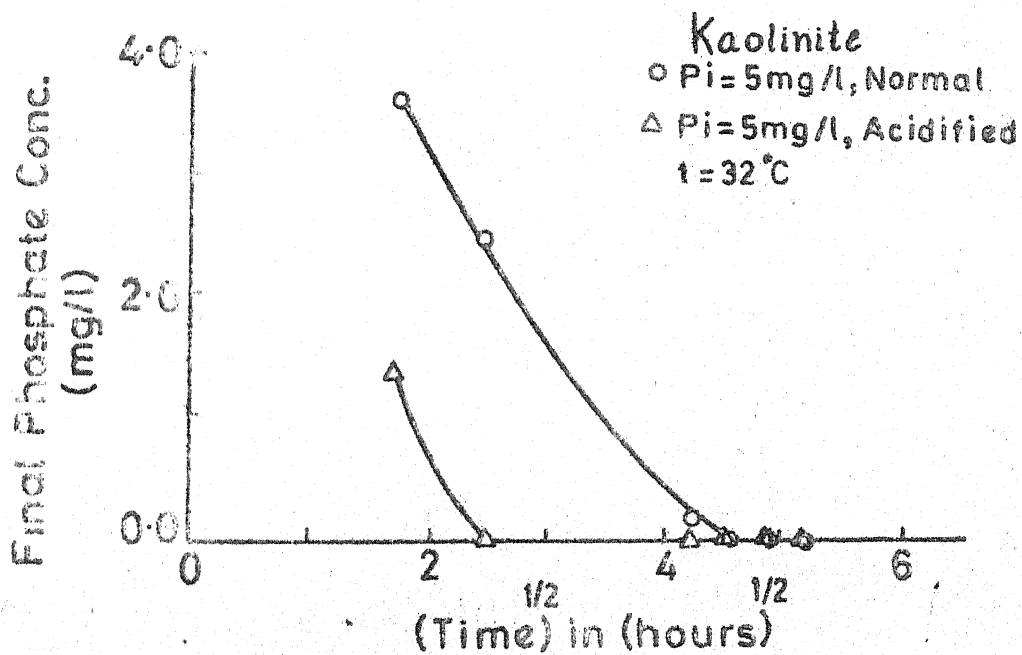


Fig. 4.23 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

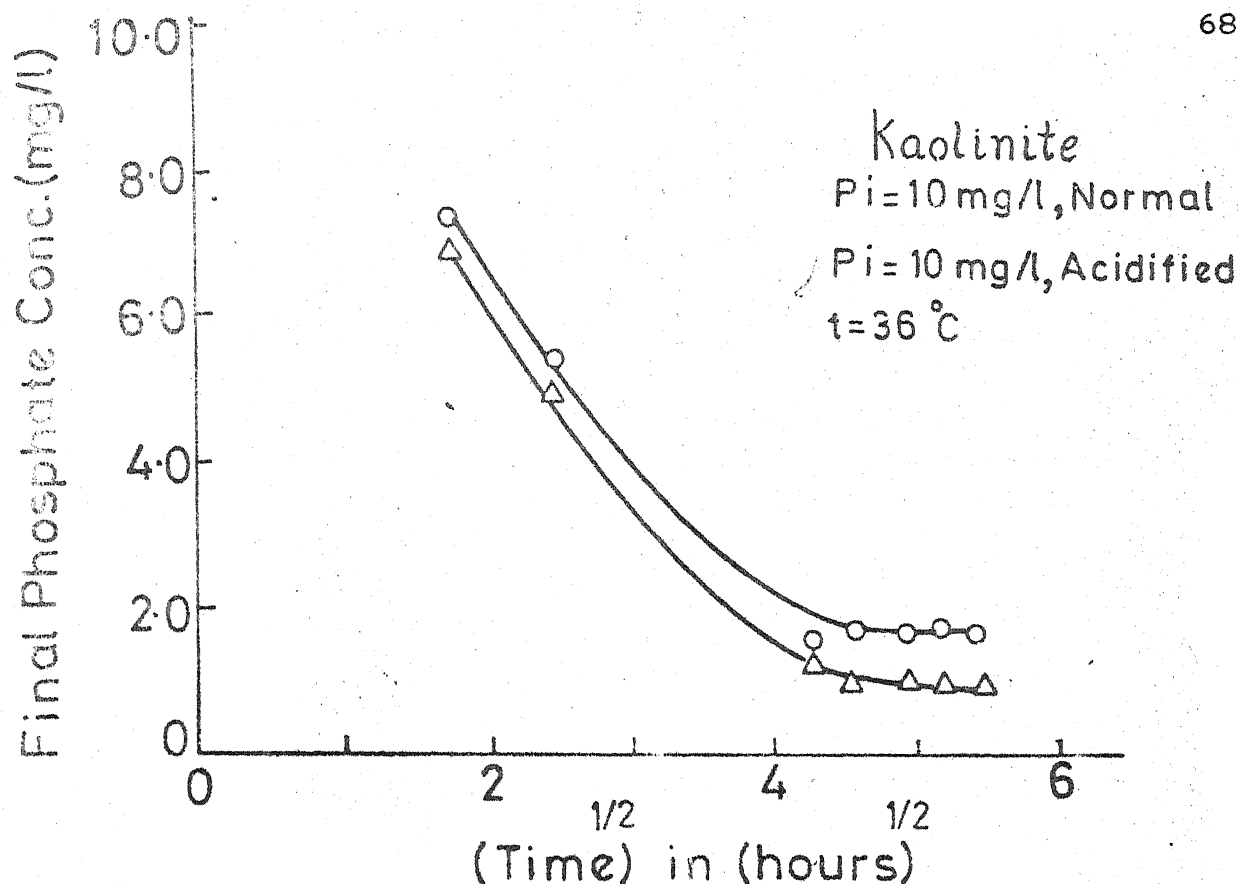


Fig. 4.24 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

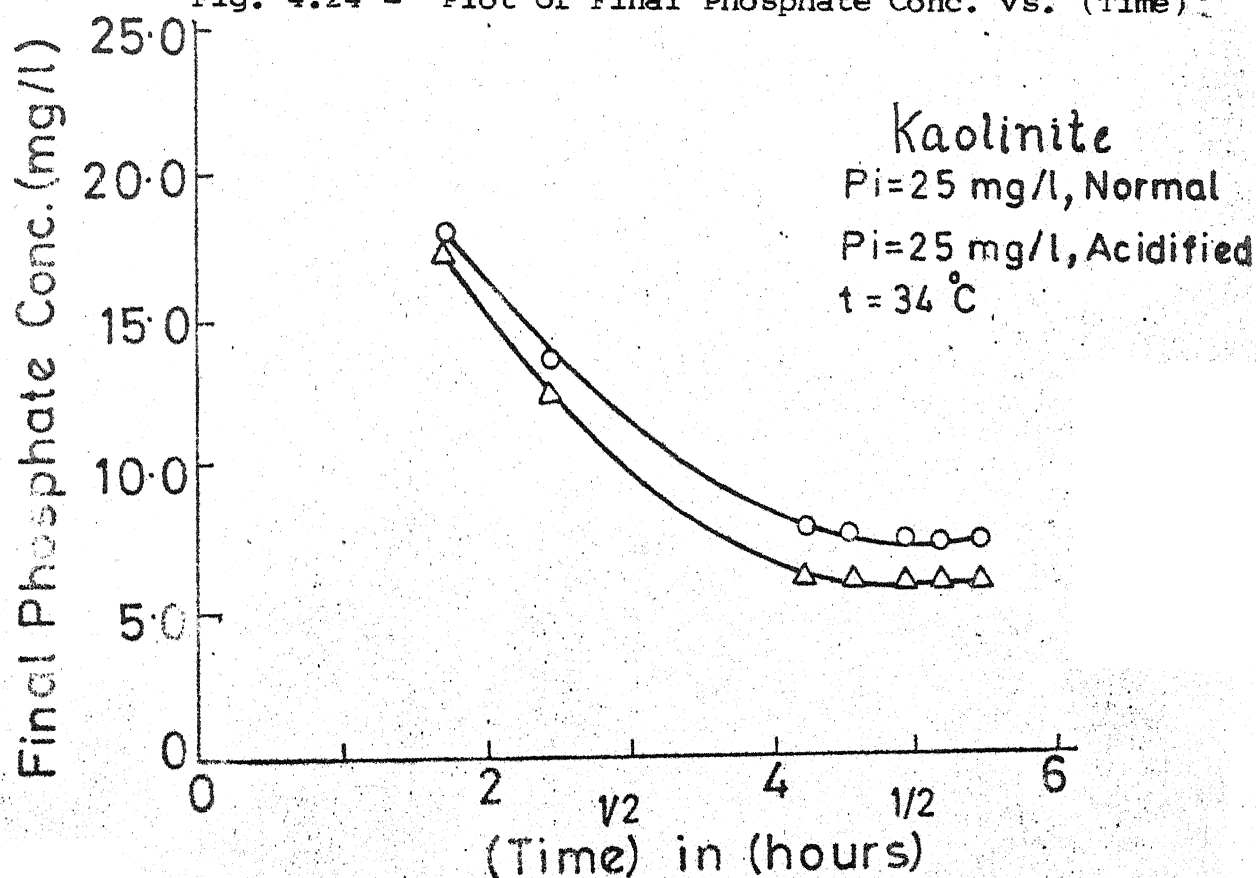


Fig. 4.25 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

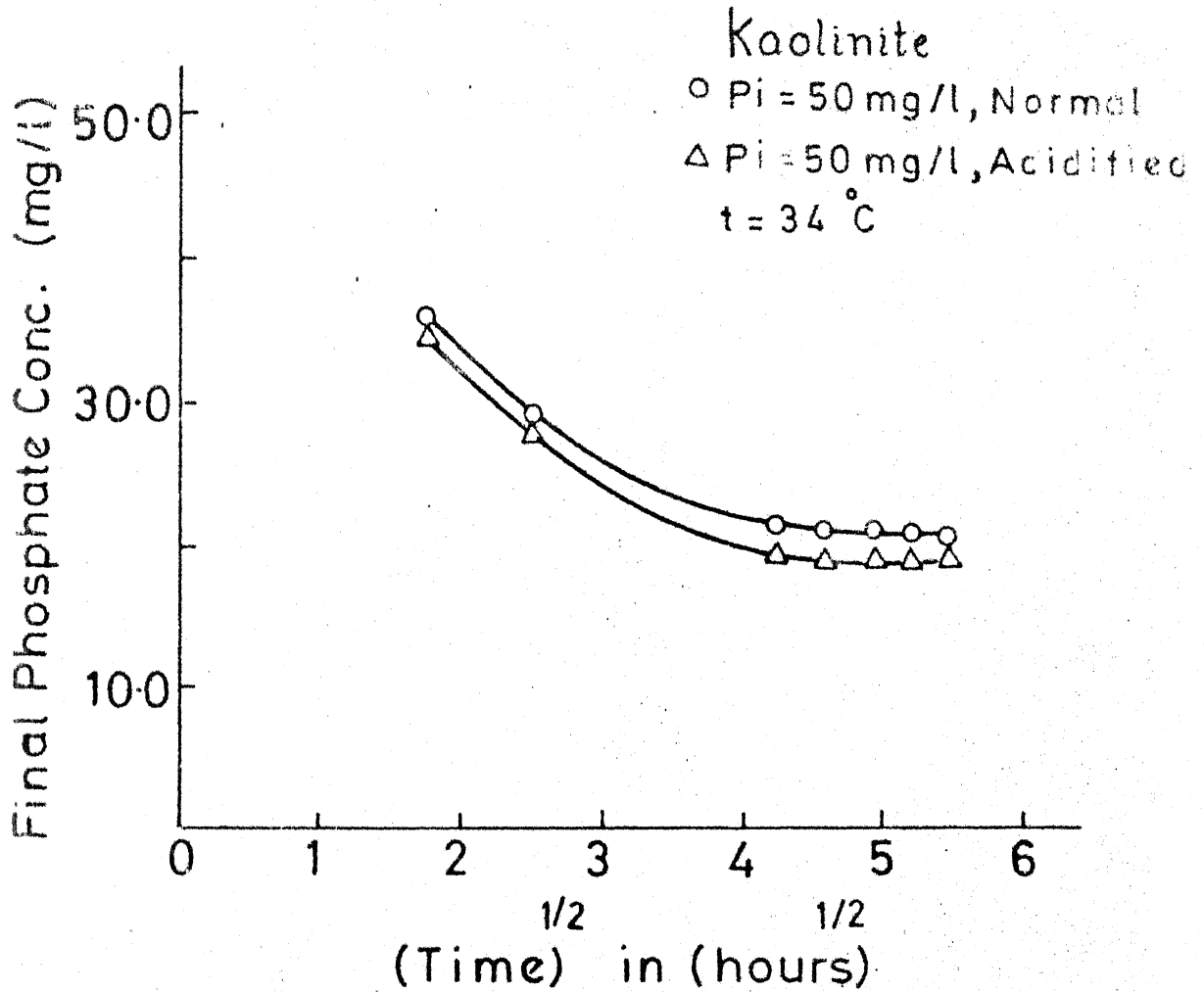


Fig. 4.26 - Plot of Final Phosphate Conc. vs. $(\text{Time})^{1/2}$

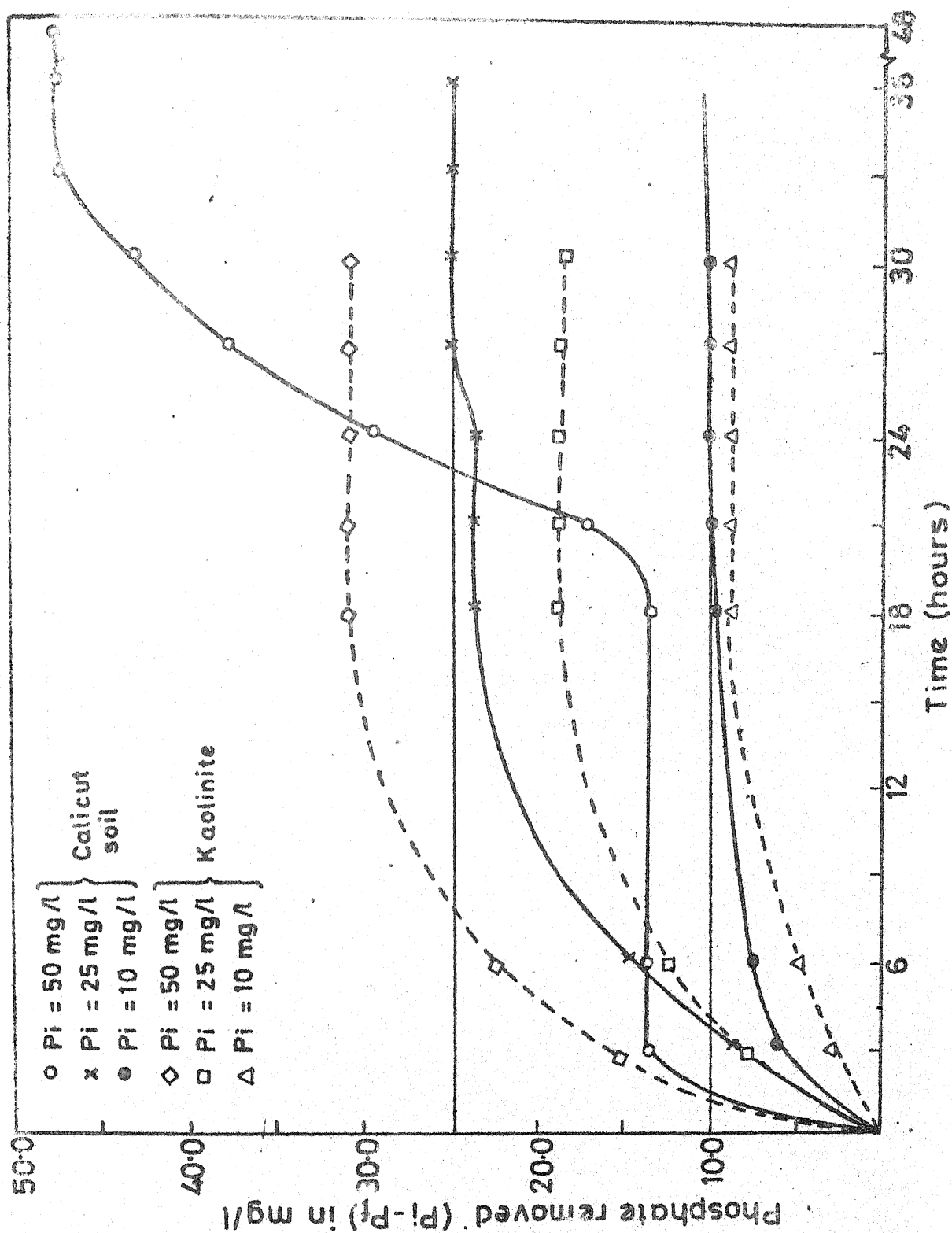


Fig. 4.27 - Phosphate Uptake by Commercial Kaolinite and Calicut Lateritic Soil.

Table 2 - Data of phosphate removal by Calicut lateritic soil ($P_i=2 \text{ mg/l}$) ($t=25^\circ\text{C}$)

NORMAL

ACIDIFIED

Contact Time	Initial PO ₄ concentration=2mg/l, pH=5.6				Initial PO ₄ concentration=2mg/l, pH:			
	Initial pH of soil + solution	Final pH of Soil+ solution	PO ₄ in solution (mg/l)	PO ₄ removed (mg/l)	Initial pH of soil + solution	Final pH of Soil+ solution	PO ₄ in solution (mg/l)	PO ₄ removed (mg/l)
3 hours	5.8	6.2	6.3	1.60	4.0	4.6	4.7	1.55
6 hours	5.8	6.3	6.3	1.15	4.0	4.8	4.9	1.05
18 hours	5.8	6.6	6.7	0.20	4.0	5.6	5.7	0.05
21 hours	5.8	6.7	6.7	0.10	4.0	5.8	5.9	0.00
24 hours	5.8	6.8	6.9	0.00	4.0	6.0	6.1	0.03
27 hours	5.8	6.8	7.0	0.00	4.0	6.1	6.2	0.13
30 hours	5.8	6.9	7.0	0.00	4.0	6.2	6.2	0.05
								1.95

Table 3 - Data of phosphate removal by Calicut lateritic soil ($P_i=5$ mg/l) ($t=27^\circ\text{C}$)

NORMAL

ACIDIFIED

Initial PO ₄ concentration=5mg/l; pH = 5.0										Initial PO ₄ concentration=5mg/l pH = 3.5									
Contact Time	Initial pH of soil+ solution	Final pH of soil+ solution	Final PO ₄ in solution (mg/l)	PO ₄ re-moved (mg/l)	Initial pH of soil+ solution	Final pH of soil+ solution	Final PO ₄ in solution (mg/l)	PO ₄ re-moved (mg/l)	Initial pH of soil+ solution	Final pH of soil+ solution	Final PO ₄ in solution (mg/l)	PO ₄ re-moved (mg/l)							
3 hours	6.6	6.9	7.0	4.15	0.85	6.0	6.0	6.1	4.0	1.0									
6 hours	6.6	7.1	7.2	3.50	1.50	6.0	6.2	6.2	3.25	1.75									
18 hours	6.6	7.4	7.6	1.00	4.00	6.0	6.3	6.4	0.65	4.35									
21 hours	6.6	7.5	7.6	0.75	4.25	6.0	6.3	6.5	0.40	4.60									
24 hours	6.6	7.7	7.8	0.25	4.75	6.0	6.5	6.7	0.00	5.00									
27 hours	6.6	7.8	7.8	0.00	5.00	6.0	6.8	7.0	0.07	4.93									
30 hours	6.6	7.8	7.8	0.00	5.00	6.0	6.7	6.9	0.07	4.93									

Table 4 - Data of phosphate removal by Calicut lateritic soil ($P_i=10\text{mg/l}$) ($t=27^\circ\text{C}$)

NORMAL

ACIDIFIED

		Initial PO_4 concentration=10mg/l; pH=4.7				Initial PO_4 concentration=10mg/l; pH=3.5			
		Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	PO_4 left in solu- tion (mg/l)	PO_4 re- moved (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	PO_4 left in solu- tion (mg/l)	PO_4 re- moved (mg/l)
3 hours	5.1	5.8	5.9	1.14	8.86	5.8	5.8	3.70	6.30
6 hours	5.1	5.8	5.9	1.00	9.00	5.8	6.1	2.25	7.75
18 hours	5.2	6.0	6.2	1.00	9.00	5.8	6.4	0.33	9.67
21 hours	5.2	6.3	6.5	0.80	9.20	5.8	6.5	0.05	9.95
24 hours	5.1	6.5	6.6	0.50	9.50	5.7	6.7	0.05	9.95
27 hours	5.1	6.7	6.8	0.20	9.80	5.8	7.0	0.03	9.97
30 hours	5.1	7.1	7.2	0.20	9.80	5.8	7.2	0.00	10.00

Table 5 - Data of phosphate removal by Calicut lateritic soil ($P_i=25$ mg/l) ($t=28^\circ\text{C}$)

ACIDIFIED

NORMAL

Initial PO_4 concentration=25mg/l;pH=4.3 Initial PO_4 concentration=25mg/l;pH=3.5											
Contact Time	Initial pH of soil+ solut-ion	Final pH of soil+ solut-ion	Initial PO_4 re-moved (mg/l)	Final PO_4 re-moved (mg/l)	Initial pH of soil+ solut-ion	Final pH of soil+ solut-ion	Initial PO_4 re-moved (mg/l)	Final PO_4 re-moved (mg/l)	Initial pH of soil+ solut-ion	Final pH of soil+ solut-ion	Initial PO_4 re-moved (mg/l)
3 hours	4.9	5.1	5.2	17.80	7.20	4.7	4.8	4.9	16.00	9.00	
6 hours	4.9	5.2	5.2	17.80	7.20	4.7	5.0	5.2	10.00	15.00	
18 hours	4.8	5.3	5.4	9.00	16.00	4.7	5.3	5.4	1.25	23.75	
21 hours	4.9	5.5	5.6	7.50	17.50	4.7	5.4	5.5	1.25	23.75	
24 hours	4.9	5.6	5.6	6.00	19.00	4.7	5.5	5.5	1.25	23.75	
27 hours	5.0	5.8	6.0	4.25	20.75	4.7	5.7	5.8	0.00	25.00	
30 hours	4.8	5.9	6.1	2.50	22.50	4.7	5.8	5.9	0.00	25.00	
33 hours	4.9	6.2	6.2	2.50	22.50	4.7	6.0	6.2	0.00	25.00	
36 hours	4.9	6.2	6.2	2.50	22.50	4.7	6.1	6.2	0.00	25.00	

Table 6 - Data of phosphate removal by Calicut lateritic soil ($P_i=50$ mg/l) ($t=25^\circ\text{C}$)

ACIDIFIED

NORMAL

Initial PO_4 concentration=50mg/l;pH=4.0 Initial PO_4 concentration=50mg/l;pH=3.5											
Contact Time	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 re- moved (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 re- moved (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 re- moved (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion
3 hours	4.5	4.8	4.9	40.0	10.0	4.2	5.6	5.8	36.0	14.0	
6 hours	4.4	5.0	5.1	40.0	10.0	4.2	6.0	6.0	36.0	14.0	
18 hours	4.5	5.2	5.2	40.0	10.0	4.2	6.1	6.2	36.0	14.0	
21 hours	4.5	5.3	5.4	32.5	17.5	4.2	6.6	6.9	32.5	17.5	
24 hours	4.5	5.5	5.6	24.0	26.0	4.2	6.9	7.1	20.0	30.0	
27 hours	4.6	5.7	5.8	16.0	34.0	4.2	7.0	7.3	12.0	38.0	
30 hours	4.5	6.0	6.2	11.0	39.0	4.2	7.1	7.4	6.5	43.5	
33 hours	4.5	6.1	6.2	10.0	40.0	4.2	7.3	7.5	2.2	47.8	
36 hours	4.5	6.1	6.3	10.0	40.0	4.2	7.4	7.5	2.0	48.0	
48 hours						4.2	7.4	7.6	2.0	48.0	

Table 7 - Efficiencies of phosphate removal from normal solutions by Calicut soil

Initial PO_4 concentration (P_i) (mg/l)	Efficiency of Removal (e) (%)	
2.0	100	
5.0	100	
10.0	98	AEC = 12.5
25.0	90	me/100g of soil
50.0	80	

Table 8 - Efficiency of phosphate removal from acidified solutions by Calicut soil

Initial PO_4 concentration (P_i) (mg/l)	Efficiency of Removal (e) (%)	
2.0	100	
5.0	100	
10.0	100	AEC = 15.00
25.0	100	me/100g of soil
50.0	98	

Table 9 - Data of phosphate removal by Varkala lateritic soil ($P_i=2$ mg/l) ($t=32^\circ\text{C}$)

	NORMAL				ACIDIFIED					
	Initial PO ₄ concentration=2mg/l;pH=5.7				Initial PO ₄ concentration=2mg/l;pH=3.5					
Contact Time	Initial pH of soil+ solution	Final pH of soil+ solution	PO ₄ left in solution (mg/l)	PO ₄ re-moved (mg/l)	Initial pH of soil+ solution	Final pH of soil+ solution	PO ₄ left in solution (mg/l)	PO ₄ re-moved (mg/l)		
3 hours	6.1	6.3	6.4	1.25	0.75	4.2	4.6	4.7	0.68	1.32
6 hours	6.1	6.5	6.6	0.80	1.20	4.2	4.8	4.9	0.48	1.52
18 hours	6.1	6.6	6.7	0.58	1.42	4.2	5.7	5.9	0.35	1.65
21 hours	6.1	6.6	6.7	0.35	1.65	4.2	5.8	6.0	0.40	1.60
24 hours	6.1	6.7	6.8	0.35	1.65	4.2	5.9	6.1	0.33	1.67
27 hours						4.2	5.9	6.0	0.30	1.70
30 hours						4.2	5.9	6.1	0.30	1.70

Table 10 - Data of phosphate removal by commercial Kaolinite ($P_i = 2 \text{ mg/l}$) ($t=34^\circ\text{C}$)

		NORMAL						ACIDIFIED					
		Initial PO_4 concentration=2mg/l; pH=5.6						Initial PO_4 concentration=2mg/l; pH=3.5					
Contact Time		Initial pH of soil+	Final pH of soil+	Initial PO_4 re-moved (mg/l)	Final PO_4 re-moved (mg/l)	Initial pH of soil+	Final pH of soil+	Initial pH of soil+	Final pH of soil+	Initial PO_4 re-moved (mg/l)	Final PO_4 re-moved (mg/l)	Initial pH of soil+	Final pH of soil+
		solut-ion	solut-ion			solut-ion	solut-ion	solut-ion	solut-ion	solut-ion	solut-ion	solut-ion	solut-ion
3 hours	5.8	5.8	5.8	1.50	0.50	3.8	4.0	3.8	4.1	0.8	1.2	3.8	4.1
6 hours	5.8	5.9	5.9	1.00	1.00	3.8	4.3	3.8	4.4	0.0	2.0	3.8	4.4
18 hours	5.8	6.2	6.3	0.05	1.95	3.8	4.6	3.8	4.7	0.0	2.0	3.8	4.7
21 hours	5.8	6.2	6.3	0.00	2.00	3.8	4.6	3.8	4.7	0.0	2.0	3.8	4.7
24 hours	5.8	6.3	6.3	0.00	2.00	3.8	4.7	3.8	4.8	0.0	2.0	3.8	4.8
27 hours	5.8	6.3	6.3	0.00	2.00	3.8	4.8	3.8	5.0	0.0	2.0	3.8	5.0
30 hours	5.8	6.3	6.4	0.00	2.00	3.8	5.2	3.8	5.3	0.0	2.0	3.8	5.3

Table 11 - Data of phosphate removal by commercial Kaolinite ($P_1 = 5 \text{ mg/l}$) ($t=32^\circ\text{C}$)

		NORMAL						ACIDIFIED					
		Initial PO_4 concentration=5mg/l;pH=5.0			Initial PO_4 concentration=5mg/l;pH=3.5			Initial PO_4 concentration=5mg/l;pH=5.0			Initial PO_4 concentration=5mg/l;pH=3.5		
Contact Time		Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 left in solu- tion (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 left in solu- tion (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 left in solu- tion (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO_4 left in solu- tion (mg/l)
3 hours	5.6	5.8	5.9	3.65	1.35	4.1	4.7	4.8	1.40	3.60	4.1	4.7	4.8
6 hours	5.6	6.1	6.2	2.50	2.50	4.1	5.6	5.8	0.10	4.90	4.1	5.6	5.8
18 hours	5.6	6.2	6.3	0.20	4.80	4.1	5.8	6.0	0.00	5.00	4.1	5.8	6.0
21 hours	5.6	6.2	6.3	0.00	5.00	4.1	6.1	6.3	0.00	5.00	4.1	6.1	6.3
24 hours	5.6	6.2	6.3	0.00	5.00	4.1	6.3	6.3	0.00	5.00	4.1	6.3	6.3
27 hours	5.6	6.3	6.3	0.00	5.00	4.1	6.3	6.4	0.00	5.00	4.1	6.3	6.4
30 hours	5.6	6.3	6.4	0.00	5.00	4.1	6.5	6.6	0.00	5.00	4.1	6.5	6.6

Table 12 - Data of phosphate removal by commercial Kaolinite ($P_i = 10 \text{ mg/l}$) ($t=36^\circ\text{C}$)

ACIDIFIED

NORMAL

		Initial PO ₄ concentration=10mg/l;pH=4.7										Initial PO ₄ concentration=10mg/l;pH=3.5									
Contact Time		Initial pH of soil+solut-ion	Final pH of soil+solut-ion	Initial PO ₄ re-moved (mg/l)	Final PO ₄ re-moved (mg/l)	Initial pH of soil+solut-ion	Final pH of soil+solut-ion	Initial PO ₄ re-moved (mg/l)	Final PO ₄ re-moved (mg/l)	Initial pH of soil+solut-ion	Final pH of soil+solut-ion	Initial PO ₄ re-moved (mg/l)	Final PO ₄ re-moved (mg/l)	Initial pH of soil+solut-ion	Final pH of soil+solut-ion	Initial PO ₄ re-moved (mg/l)	Final PO ₄ re-moved (mg/l)				
3 hours	4.9	5.4	5.5	7.5	2.5	4.0	4.7	4.8	7.00	3.00											
6 hours	4.9	5.5	5.7	5.5	4.5	4.0	4.8	4.8	5.00	5.00											
18 hours	4.9	5.8	5.9	1.5	8.5	4.0	5.1	5.2	1.27	8.75											
21 hours	4.8	6.0	6.1	1.8	0.2	4.0	5.2	5.4	1.00	9.00											
24 hours	4.9	6.1	6.2	1.7	9.3	4.0	5.3	5.4	1.00	9.00											
27 hours	4.9	6.1	6.2	1.8	8.2	4.0	5.5	5.7	1.00	9.00											
30 hours	4.9	6.2	6.2	1.8	8.2	4.0	5.5	5.0	1.00	9.00											

Table 13 - Data of phosphate removal by commercial Kaolinite ($P_i = 25 \text{ mg/l}$) ($t=34^\circ\text{C}$)

		ACIDIFIED									
		NORMAL									
		Initial PO ₄ concentration=25mg/l,pH=4.3 Initial PO ₄ concentration=25mg/l;pH=3.5									
Contact Time		Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO ₄ left in solu- tion (mg/l)	PO ₄ re- moved (mg/l)	Initial pH of soil+ solut- ion	Final pH of soil+ solut- ion	Final PO ₄ left in solu- tion (mg/l)	PO ₄ re- moved (mg/l)		
3 hours	4.5	4.8	4.9	18.0	7.0	4.3	4.3	4.3	17.00	8.00	
6 hours	4.5	5.0	5.2	13.8	11.2	4.3	4.5	4.6	12.50	12.50	
18 hours	4.5	5.4	5.5	8.0	17.0	4.3	4.7	4.8	6.25	18.75	
21 hours	4.5	5.6	5.8	7.8	17.2	4.3	4.8	5.0	6.00	19.00	
24 hours	4.5	5.7	5.8	7.5	17.5	4.3	5.1	5.3	6.00	19.00	
27 hours	4.5	5.8	6.0	7.4	17.6	4.3	5.3	5.4	6.00	19.00	
30 hours	4.5	5.8	6.1	7.5	17.5	4.3	5.5	5.5	6.00	19.00	

Table 14 - Data of phosphate removal by commercial Kaolinite ($P_i = 50 \text{ mg/l}$) ($t=34^\circ\text{C}$)

NORMAL ACIDIFIED

		Initial PO_4 concentration=50mg/l;pH=4.0 Initial PO_4 concentration=50mg/l;pH=3.5									
Contact Time		Initial pH of soil+	Final pH of soil+	Initial PO_4 re-	Final PO_4 re-	Initial pH of soil+	Final pH of soil+	Initial PO_4 re-	Final PO_4 re-	Initial pH of soil+	Final pH of soil+
		solut-ion	solut-ion	moved (mg/l)	moved (mg/l)	solut-ion	solut-ion	moved (mg/l)	moved (mg/l)	solut-ion	solut-ion
3 hours	4.2	4.3	4.4	36.00	14.00	4.6	4.6	4.6	4.6	35.0	15.0
6 hours	4.2	4.4	4.5	29.00	21.00	4.6	4.8	5.0	28.0	22.0	
18 hours	4.2	4.6	4.8	21.45	28.55	4.6	5.6	5.7	19.0	31.0	
21 hours	4.2	4.7	4.8	21.00	29.00	4.6	5.6	5.7	19.0	31.0	
24 hours	4.2	4.7	4.8	21.45	28.55	4.6	5.7	5.7	19.0	31.0	
27 hours	4.2	4.8	4.9	21.00	29.00	4.6	5.7	5.8	19.0	31.0	
30 hours	4.2	4.9	5.0	21.00	29.00	4.6	5.8	5.8	19.0	31.0	

Table 15 - Efficiencies of phosphate removal from normal solutions by kaolinite

Initial PO ₄ concentration (P _i) (mg/l)	Efficiency of Removal (e)	
2.0	100	
5.0	100	
10.0	82	AEC = 9.06
25.0	70	me/100g of soil
50.0	58	

Table 16 - Efficiencies of phosphate removal from acidified solutions by kaolinite

Initial PO ₄ concentration (P _i) (mg/l)	Efficiency of Removal (e)	
2.0	100	
5.0	100	
10.0	90	AEC = 9.68
25.0	76	me/100g of soil
50.0	62	

CHAPTER V - CONCLUSIONS AND FURTHER WORK

5.1. CONCLUSIONS:

The following conclusions may be drawn from the present study:

- (1) Calicut lateritic soil is definitely better suited than commercial kaolinite for phosphate uptake. It has an efficiency of 98 to 100 percent in the temperature range of 25 to 28°C. Varkala lateritic soil, on the other hand is much less efficient at the same soil to solution ratio at 33°C.
- (2) Presence of abundant iron oxides made the Calicut soil more efficient for phosphate uptake. Positive charge over iron oxides surfaces was found to be responsible for the observed high phosphate uptake capacities. Lesser proportion of iron oxides and clay minerals in Varkala lateritic soil together with high quartz and feldspar contents made it comparatively inefficient.
- (3) Kinetic interpretations of the removal data showed four stages: (1) Instantaneous removal on surface sites of iron oxides and clay minerals, (2) Saturation of these sites and the first equilibrium stage, (3) Gradual removal into the interlamellar sites of halloysite, and (4) Saturation with final equilibrium stage.
- (4) In commercial kaolinite, phosphate uptake was restricted to the edges of the particles.

- (5) Due to acidification of the solutions, increase in the phosphate uptake capacity was more for Calicut lateritic soils than Kaolinite.
- (6) Varkala lateritic soil showed an improvement^V in its uptake efficiency, on increasing soil to solution ratio.

5.2. SCOPE FOR FURTHER WORK:

For a complete understanding of the process of phosphate removal by lateritic soils, several factors in addition to pH, initial phosphate concentration and contact time can be investigated:

- (1) More detailed information is required on the effect of soil to solution ratio. The single experiment with Varkala soil in this work indicates this to be an important parameter.
- (2) These experiments were conducted with a uniform grain size of the soils (Sieved in the range of 0.18 to 0.25 mm). Literature review shows that surface adsorption depends strongly on grain size of the adsorbant particles. It is expected that removal will increase with decrease in grain size of the soils, but may have an optimum size for maximum efficiency. This fact should be verified by proper experiments.

- (3) Commercial feasibility of adsorption reactions would also depend on subsequent desorption down concentration gradients. It is important to tabulate the adsorption-desorption fractions of phosphate removal by lateritic soil.
- (4) The change in mineral structure, if any, after adsorption can be studied by the X-ray and DTA pattern of the soil after desorption. The part held permanently by the mineral may cause expansion of lattice and thermal effects
- (5) Although phosphate was selected in the present experiments for its double role in pollution and fertilizer application, it is obvious that the removal mechanism will be better understood if similar experiments are conducted with other anions like F^- , NO_3^- or organic substances e.g. dyes and detergents.

LIST OF FIGURES

	<u>Page</u>
2.1 . Structure of clay minerals	19
2.2 . Schematic Diagram of Dual charge on a Kaolinite particle	20
3.1 . Typical standard curve for phosphate determination	25
4.1 . Geological Map of Kerala showing outcrops of Laterites	48
4.2 . Sketch of Microscopic view of Coarser fraction of Calicut soil after acid washing	49
4.3 . Sketch of X-ray Diffraction pattern of Calicut soil	50
4.4 . Sketch of Microscopic view of Coarser fraction of Varkala soil after acid washing	51
4.5 . Sketch of X-ray Diffraction pattern of Varkala soil	52
4.6 . DTA and TG patterns of Varkala soil	53
4.7 . Phosphate uptake by Calicut soil, $P_i = 2, 5$ mg/l	54
4.8 . Phosphate uptake by Calicut soil, $P_i = 10, 25, 50$ mg/l	55
4.9 . Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Calicut soil-phosphate system, $P_i = 2$ mg/l	56
4.10. Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Calicut soil-phosphate system, $P_i = 5$ mg/l	56
4.11. Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Calicut soil-phosphate system, $P_i = 10$ mg/l	57
4.12. Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Calicut soil-phosphate system, $P_i = 25$ mg/l	57
4.13. Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Calicut soil-phosphate system, $P_i = 50$ mg/l	58
4.14. Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for various initial phosphate levels. (Calicut soil normal phosphate solution system)	59

4.15.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for various initial concentrations (Calicut soil-acidified phosphate solution system)	60
4.16.	Extrapolated adsorption isotherm (Calicut soil-phosphate system)	61
4.17.	Phosphate uptake by Varkala soil, $P_i = 2 \text{ mg/l}$	62
4.18.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Varkala soil-phosphate system, $P_i = 2 \text{ mg/l}$	63
4.19.	Sketch of X-ray Diffraction Pattern of commercial Kaolinite	64
4.20.	Phosphate uptake by Commercial Kaolinite, $P_i = 2.5 \text{ mg/l}$	65
4.21.	Phosphate uptake by Commercial Kaolinite, $P_i = 10, 25, 50 \text{ mg/l}$	66
4.22.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Kaolinite-phosphate system, $P_i = 2 \text{ mg/l}$	67
4.23.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Kaolinite-phosphate system, $P_i = 5 \text{ mg/l}$	67
4.24.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Kaolinite-phosphate system, $P_i = 10 \text{ mg/l}$	68
4.25.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Kaolinite-phosphate system, $P_i = 25 \text{ mg/l}$	68
4.26.	Plot of final phosphate concentration vs. $(\text{Time})^{\frac{1}{2}}$ for Kaolinite-phosphate system, $P_i = 50 \text{ mg/l}$	69
4.27.	Phosphate uptake by commercial Kaolinite and Calicut lateritic soil.	70

LIST OF TABLES

	<u>Page</u>
1. Anion Exchange Capacity of Clay Minerals	12
2. Data of Phosphate removal by Calicut lateritic soil, $P_i = 2$ mg/l	71
3. Data of phosphate removal by Calicut lateritic soil, $P_i = 5$ mg/l	72
4. Data of phosphate removal by Calicut lateritic soil, $P_i = 10$ mg/l	73
5. Data of phosphate removal by Calicut lateritic soil, $P_i = 25$ mg/l	74
6. Data of phosphate removal by Calicut lateritic soil, $P_i = 50$ mg/l	75
7. Efficiencies of phosphate removal by Calicut soil from normal solutions	76
8. Efficiencies of phosphate removal by Calicut soil from acidified solutions	76
9. Data of phosphate removal by Varkala lateritic soil, $P_i = 2$ mg/l	77
10. Data of phosphate removal by commercial Kaolinite, $P_i = 2$ mg/l	78
11. Data of phosphate removal by commercial Kaolinite, $P_i = 5$ mg/l	79
12. Data of phosphate removal by commercial Kaolinite, $P_i = 10$ mg/l	80
13. Data of phosphate removal by commercial Kaolinite, $P_i = 25$ mg/l	81
14. Data of phosphate removal by commercial Kaolinite, $P_i = 50$ mg/l	82
15. Efficiencies of phosphate removal by Kaolinite from normal solutions	83
16. Efficiencies of phosphate removal by Kaolinite from acidified solutions	83

REFERENCES

1. Bates, T.F., F.A. Hildebrand and A. Swineford, (1950); Morphology and Structure of Eudellite and Halloysite., Am. Mineralogist, 35, pp:463-484.
2. Bowden, J.W., Bolland, M.D.A., Posner, A.M. and Quirk, J.P., (1974); Generalised model for anion and cation adsorption on oxide surfaces, Nature (London), 245, pp:81-82.
3. Carroll, D., (1959); Ion exchange in clays and other minerals, Bull. Geol. Soc. Am., 70, pp:749-780.
4. Drewry, William A., and Eliassen, R., (1968); virus movement in ground water, JWPCF, 40, Research Supplement, pp:257-271.
5. Fink, D.H., Thomas, G.W. and Meyer, W.J., (1970); Adsorption of anionic detergents by soils, JWPCF, 42, pp:265-272.
6. Fruh, F.G., (1967); 'The overall picture of eutrophication'; JWPCF, 39, pp:1449-1463.
7. Gast, R.G. (1977); surface and colloid chemistry, Ch. 2 in 'Minerals in Soil Environment', edited by Dixon, J.B. et al, Soil Sci. Soc. Am. Publications, Medison, Wisconsin.
8. Gidigas, M.D., (1976); Laterite Soil Engineering, Elsevier Scientific Publishing Company, New York.
9. Grim, R.E., (1953); Clay Mineralogy, McGraw Hill Book Co., New York.
10. Huang, J. and Liao, C. (1970); Adsorption of pesticides by clay minerals, Jour. Sanitary Engg. Division, Proc. Am. Soc. Civil Eng., 96, pp:1057-1078.
11. Kittrick, J.A. and Jackson, M.L., (1956); Electron Microscope observations of the reaction of phosphates with minerals, leading to a unified theory of phosphate fixation in soils, Jour. Soil Sci., 7, pp:81-89.
12. Koya, K.V. Abdulla and Chaudhuri, Malay (1976); virus retention by soil, Progress in Water Tech., 9, pp:53-63, Paragon Press, Great Britain.
13. Krauskopf, K.B., (1967); Introduction To Geochemistry, McGraw Hill, New York.

14. Kuo, S. and Mikkelsen, D.S., (1979); Distribution of Iron phosphorus in flooded and unflooded soil profiles and their relation to phosphorous adsorption, Soil Sci., 127, pp: 18-25.
15. Malikarjuna, C., Vidhyadharan, K.T., Pawar, S.D., Senthia M. and Francis, P.G., (1979); Geological, geochemical and geotechnical aspects of the laterites of Kerala. Proc. Inter. Seminar on Lateritisation Processes, Trivandrum, pp: 425-435.
16. Marshall, C.E., (1949); The Colloid Chemistry of the Silicate Minerals, Academic Press Inc., New York.
17. McLaughlin, J.R., Ryden, J.C. and Syers, J.K., (1981); Sorption of Inorganic phosphate by Iron and Aluminium containing components, Jour. Soil Sci., 32, pp:365-37
18. Orme, E.D. and Nelson, D.W., (1979); chemistry of phosphor cadmium, copper, Nickel, Lead and Zinc in Indiana lake and Reservoir Sediments, Technical Report No. 122, Purdue University Water Resources Research Centre, West Lafayette, Indiana.
19. Pandey, M.P. and Chaudhuri, Malay (1980); 'Inorganic Mercury-Bituminous Coal Sorption Interactions in Water, Progress Water Tech., 12, Toronto, pp:697-711.
20. Pendelton, R.L. and Sharda-suvana, S., (1946); Analysis of some Siamese laterites, Soil Sci., 62, pp: 423-440.
21. Rao, K.S. and Raymahashay, B.C., (1981); Influence of clay minerals and iron oxides on selected properties of two lateritic soils, Indian Geotech. Jour., 11, pp: 255-266.
22. Robson, A.D. and Gilkes, R.J., (1979); fertilizer responses (N,P,K,S. micronutrients) on lateritic soils in SW Australia - a review, Proc. International Seminar on Lateritisation Processes, Trivandrum, pp: 381-390.
23. Sadhukhan, N.C. and Raymahashay, B.C., (1972); A parametric evaluation of phosphate removal by Alum coagulation, Ind. Jour. Env. Health, 14, pp: 337-346.
24. Schwertmann, U. and Taylor, R.M., (1977); Iron oxides, Ch.5 of Minerals in Soil Environment, edited by Dixon, J.B. et al, Soil Sci. Soc. Am. Pub., Madison, Wisconsin.

25. Sethuraman, V.V., and Raymahashay, B.C., (1975); color removal by clays; kinetic study of adsorption of cationic and anionic dyes, *Env. Sci. & Tech. (Am. Chem. Soc.)*, 9, pp: 1139-1140.
26. Sethuraman, V.V. and Raymahashay, B.C., (1980); Adsorption and desorption studies of cationic and anionic dyes on clay minerals and application to colour removal, *Jour. Inst. of Engineers (India)*, 61, pt EN1, pp: 19-23.
27. Sree Ramalu, U.S., Pratt, P.F. and Page, A.L., (1967); P fixation by soils in relation to extractable iron oxides and mineral composition, *Soil Sci. Soc. Am. Proc.*, 31, pp: 193-196.
28. Summer, M.E., (1962); Effect on iron oxides on positive and negative charges in clays and soils, *clay Mineral Bull.*, 5, pp: 218-226.
29. Train, R.E., (1979); 'Quality Criteria for Water', Castle House Publications Ltd. Guildford.
30. Van Olphen, H., (1963); An Introduction To Clay Colloid Chemistry, Interscience Publishers, New York.
31. Wayman, C.H., (1967); 'Adsorption on clay mineral surfaces' In Principles and Applications of Water Chemistry, Edited by Faust, S.D. and Hunter, J.V., *Proc. 4th Rudolfs Res. Conf.*, John Wiley and Sons, Inc, New York.
32. Weber, W.J., Jr.; and Morris, J.C., (1963); Kinetics of adsorption on carbon from solution, *J. Sanitary Engg. Div., Proc. Am. Soc. Civ. Eng.*, 89, pp: SA2, 31-59.
33. Weber, W.J. and Gould, J.P., (1966); Sorption of organic pesticides from aqueous solutions, in 'Organic Pesticides in Environment', Gould R.F. ed., *American Chemical Society Advance in Chemistry Sr. No. 60*, Washington, D.C., pp: 280-304.
34. Wild. A., (1950); The retention of phosphates by soils-a review, *Jour. Soil Sci.*, 1, pp:221-238.
35. Yariv, S. and Cross, H., (1979); 'Geochemistry of Colloid Systems for Earth Scientists' Springer-Verlag, New York.